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# Ferric & Heliographic Processes.

**George E. Brown    F.I.C.**



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# Ferric & Heliographic Processes:

A Handbook for Photographers,  
Draughtsmen, and Sun Printers

By GEORGE E. BROWN, F.I.C.

(Late of the G. W. Railway Co. Chemical Staff;  
Joint-Editor of "The Photogram")

SECOND EDITION


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PUBLISHED FOR THE PHOTOGRAM, LTD.

BY

DAWBARN & WARD, LTD.

6 FARRINGTON AVENUE, LONDON, E.C.

A faint, stylized illustration in the background. On the left, a circular Ferris wheel with many spokes is visible. To the right of the wheel is a tall, slender vertical structure, possibly a lighthouse or a tower, with a small rectangular section near the top. The entire scene is rendered in a light, sketchy style.

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## INTRODUCTION

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THIS little handbook is intended to serve two classes of people. First, amateur photographers, with a taste for experiment, who may find in the preparation of their own sensitive papers much interesting work; and, secondly, draughtsmen, engineers, architects, surveyors, and others, who find the reproduction of tracings and drawings a matter of every-day necessity.

It would have been easy to have made the manual greatly exceed its present proportions; but the writer has preferred to omit any notice of those processes, the difficulty or unreliability of which only makes their employment disappointing. Much, too, that might have been said on theoretical matters is omitted, the aim of the book being to be strictly practical.

Mr W. E. Brewerton has kindly supplied particulars of the process described in Chapter IV.

## PREFACE TO SECOND EDITION.

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REVISIONS and additions have been made as called for by the expansion of the subject. The writer believes that the volume as it now stands represents our current knowledge of these iron printing processes and their technical uses.

# CONTENTS

CHAP.	PAGE
I. THE FERRO-PRUSSATE PROCESS, . . .	11
II. TONING BLUE PRINTS, . . . . .	17
III. THE USES OF BLUE PRINTS, . . . . .	23
IV. FERRO-PRUSSATE IN TRI-COLOR WORK, . . .	29
V. THE KALLITYPE PROCESS, . . . . .	32
VI. THE OBERNETTER PROCESS, . . . . .	45
VII. THE URANOTYPE PROCESS, . . . . .	49
VIII. PRINTS ON FABRICS—PRINTS IN DYES, . . .	53
IX. HELIOGRAPHIC PROCESSES COMPARED, . . .	56
X. PREPARATION OF HELIOGRAPHIC PAPERS, . . .	59
XI. MAKING TRACINGS FOR SUN-COPYING, . . .	75
XII. OUTFIT FOR HELIOGRAPHIC PRINTING, . . .	77
XIII. FERRO-PRUSSATE, OR WHITE LINE ON BLUE GROUND,	90
XIV. PELLET, OR BLUE LINE ON WHITE GROUND, . .	94
XV. FERRO-GALLIC, OR BLACK LINE ON WHITE GROUND,	99
XVI. BROWN LINE ON WHITE GROUND, . . . . .	102
XVII. MINOR HELIOGRAPHIC PROCESSES, . . . . .	105

CHAP.	PAGE
XVIII. PRINTING HOUSE MEMORANDA, . . . .	115
XIX. MANIPULATION, . . . .	117
XX. PAPER AND SIZING, . . . .	126
XXI. CHEMICALS, . . . .	132
XXII. CHEMISTRY, . . . .	139
BIBLIOGRAPHY, . . . .	146
INDEX, . . . .	148

# FERRIC AND HELIOGRAPHIC PROCESSES

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## CHAPTER I

### THE FERRO-PRUSSATE PROCESS

*Theory in Brief.*—Paper is coated with a mixture of ferric salt and potassium ferricyanide: on exposure to light, the ferric salt is reduced to ferrous salt, which gives, with the ferricyanide, a precipitate of Turnbull's blue.

The ferro-prussiate can claim to be one of the oldest printing processes, for it was used by Herschel, in substantially its present form, in 1840. For simplicity and permanency it is second to none. The color of its image is not one which fits the process for regular and systematic use; but many subjects, particularly seascapes and cloudscapes, river and lake scenery, and others, into the composition of which water enters, are admirably suited for reproduction by the blue process. The color of the blue image can be altered in various ways, though not always with the most satisfactory results.

The paper for blue printing is best sensitised at home rather than bought ready-made. The amateur may not be able to make a paper that will keep a long time, but he will have no difficulty at all in preparing one that will give far better results than much of the paper obtained in commerce.

Here, then, is a simple and easily-worked formula. Make two solutions :—

- |                               |            |            |
|-------------------------------|------------|------------|
| (1) Ferric am. citrate (red), | 80 grains. | 183 grams. |
| Water,                        | 1 ounce.   | 1000 c.cs. |
| (2) Potass ferricyanide,      | 60 grains. | 137 grams. |
| Water,                        | 1 ounce.   | 1000 c.cs. |

Unless the ferricyanide crystals are pure ruby red, wash them for a moment or two in a little water, as directed on page 138, before weighing. When the two salts have been separately dissolved, mix the two solutions in a stone bottle (previously well cleaned), or in a bottle encased in a light-tight tin, and keep well corked. The mixed solution works better after a week or so : giving a softer-working and more rapid paper. It will keep in the dark for a long time (months), but requires filtering just before use. This is an important point, and should on no account be omitted, even if the solution has been recently mixed. The filtration need only take a minute or two, provided a suitable filter paper and funnel is used, and the former properly fitted (see page 119).

If a little bichromate of potash be dissolved in the sensitising solution—in the proportion of half a grain per ounce or one gram per litre—the paper will keep considerably longer than if prepared with the plain

mixture ; but paper is so very readily coated that this addition is not really necessary.

As explained in the chapter on paper, a very great variety of papers can be coated with the sensitising solution, if a good arrowroot sizing be first given. The beginner will find it best to use a thin paper like Rives, which does not absorb too much sensitiser. Pin the sheets down to a clean board, placing a piece of blotting-paper underneath, and coat the paper as evenly as possible with a fine Turkish sponge. You will find it quite easy to give a very uniform coating. Coating the paper must, of course, take place by gas-light or very weak daylight, as used for toning. The paper must be dried as quickly as possible in the dark—in a drying-cupboard or at a moderate distance from the fire. It should be kept as dry as possible. As to how long the sensitised paper will keep in good condition, a great deal depends on the quality of the paper and on the sizing. Good paper lightly sized keeps longest, whilst a low-grade paper with heavy sizing speedily deteriorates.

On exposure to light behind a negative, the color of the paper gradually changes through bluish-green and bluish-grey to olive-green. A fully exposed print has a choked-up appearance in the shadows, whilst, with some papers, excessive over-exposure produces a peculiar bleached appearance of the shadows. On removal from the frame, the print can be kept for a day or two, though it is better to develop within a few hours.

Development consists in merely washing the print in water till the soluble salts are removed. The

process may be assisted by gently rubbing with a soft sponge. Many waters contain carbonate of lime in solution, which gradually decomposes Turnbull's blue, so that as short a washing as possible, commensurate with removing the soluble salts, is to be aimed at. Half an hour to an hour in frequent changes is ample, but with some waters it is not possible to give this without distinctly weakening the prints. In these cases a little citric acid (20 grains per pint) should be added to the wash waters to counteract their alkalinity; then a final washing in two or three changes of plain water.\* A paper which prints very much more quickly, and is just as satisfactory in other ways, is made by coating with a mixture containing green ferric ammonium citrate instead of the red. This salt, the use of which is due to Valenta, can be had from Merck, of Jewin Street. Two solutions are made as before :—

Ferric am. citrate (green),	110 grains.	250 grams.
Water, . . . . .	1 ounce.	1000 c.cs.
Potass ferricyanide, . . . . .	40 grains.	90 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

Equal volumes, mixed together, make the sensitising solution, which keeps just as well as that made with red citrate.

A still more rapid paper is prepared in an entirely

\* A mixture of alcohol (50 parts) and water (950 parts) is recommended by Hofbauer (*Camera Obscura*, 1899, p. 288) in place of pure water, as giving prints with pure whites. For deep blue shadows, the prints are transferred direct from the alcohol bath to a 2 per cent. potass bichromate solution. After remaining here a few minutes they are rinsed in 1 : 50 acetic acid and dried.



different way. Uranic salts, when exposed to light, are reduced to uranous salts, and if the exposure takes place in the presence of a ferric salt, the uranous salt reduces the ferric salt to the ferrous state, becoming itself thereby oxidised back to uranic salt, and ready to be affected by light again. This action, coupled with the direct action of light on ferric salts, confers upon paper coated with a mixture of the two salts a high degree of sensitiveness. Papers prepared in accordance with these facts were described by Alleyne Reynolds before the Sheffield Photographic Society in 1889, but appear to have attracted little attention. Reynolds' formula for coating was a mixture of equal volumes of a saturated solution of uranic chloride and a 40 per cent. solution of ferric sodic oxalate. A simpler formula, which the writer finds to answer very well, is:—

Green ferric am. citrate, .	110 grains.	250 grams.
Uranic nitrate, . . .	35 „	80 „
Water, . . . . .	1 ounce.	1000 c.cs.

This is applied to paper in the usual way, and prints in the frame to a rather faint image, which is developed on a solution of potassium ferricyanide:—

Potass ferricyanide, . . .	22 grains.	50 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

The blue image at once makes its appearance, and the print has only to be washed in water in the usual way.

A large number of formulæ for the ferro-prussiate process have been published, and while for simplicity and certainty the writer can recommend the foregoing, one or two others may be added.

Chambon\* gives :—

Gum arabic, . . .	88 grains.	200 grams.
Ferric am. citrate, . .	131 „	300 „
Tartaric acid, . . .	88 „	200 „
Distilled water, . . .	2 ounces.	2000 c.cs.

Dissolve completely, and add :—

Liq. ammonia, . . .	192 mins.	400 c.cs.
---------------------	-----------	-----------

Shake well, and add :—

Potass ferricyanide, . .	110 grains.	250 grams.
Distilled water, . . .	1 ounce.	1000 c.cs.

Mix thoroughly, and allow to stand a quarter of an hour before use. The color of the prints is improved by—

Eau-de-javelle, † . . .	25 mins.	50 c.cs.
Water, . . . . .	1 ounce.	1000 „

followed by thorough washing.

Lagrange ‡ gives :—

Ferric am. oxalate, . .	44 grains.	100 grams.
Oxalic acid, . . . .	4 „	10 „
Distilled water, . . .	1 ounce.	1000 c.cs.
Potass ferricyanide, . .	44 grains.	100 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

Use equal parts.

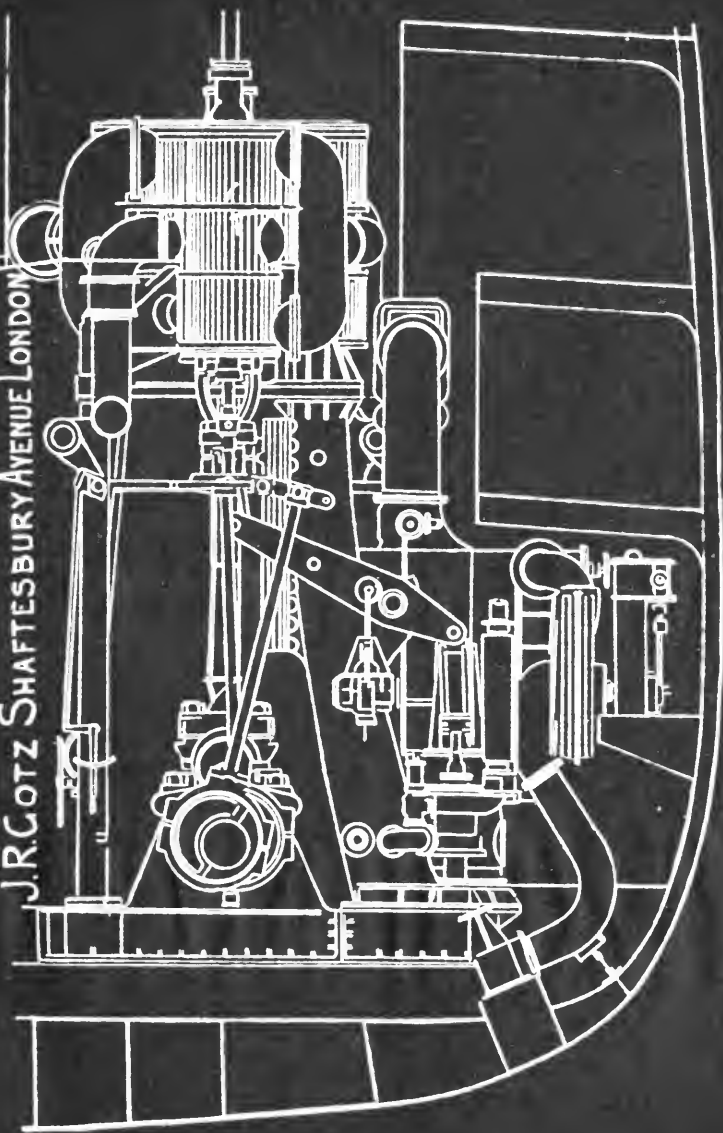
Other formulæ, especially for engineering work, will be found in Chapter X.

\* *The British Journal of Photography*, 16th Dec. 1898.

† Or, Labarraque's solution (sodium hypochlorite) is made as follows:—Shake up bleaching powder (1 ounce) with crystallised soda carbonate (1½ ounces), previously dissolved in a little water. Filter. Shake up undissolved residue with plain water, and again filter. Use filtrate. (*The Figures, Facts, and Formulæ of Photography*).

‡ *Phot. Wochenblatt*, 1887, p. 418.

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## CHAPTER II

## TONING BLUE PRINTS

BLUE prints can be toned to several other colors, and a large number of formulæ have been published at one time or another. Many of these do not come within the sphere of practical photography, for they merely enable a tone to be obtained which is very frequently only a sorry apology for one which can be obtained much more readily by some other process. For instance, the Kallitype and Obernetter processes give dark rich tones very easily, and it is a mistaken policy to torture the blue ferro-prussiate image with chemical reagents, with the object of imitating these other processes.

The most satisfactory processes for altering the color of blue prints will now be given, premising the remark that, for success, the prints must be well washed, and have been made on well-sized paper, to avoid a sunken image.

*Greenish-black (Roy's process).*—Make a solution of—

Borax,	.	.	.	30 grains.	70 grams.
Water,	.	.	.	1 ounce.	1000 c.cs.

Add drop by drop sulphuric acid till the solution reddens litmus-paper. Then add 10 per cent. ammonia solution until the red color of the litmus-paper just commences to change; if too much ammonia is added, add one or two drops more sulphuric acid and try again. The liquid should just show a faint alkaline reaction. Now add—

Powdered catechu, .      4 grains.      10 grams,

and shake well. Nearly all the catechu dissolves. The solution is filtered and is ready for use. The washed print is placed in the above solution and removed at the stage desired. Catechu occurs in commerce in several varieties,\* and the tone varies with them, ranging from greenish-blue to greenish-black. Keep the solution as cold as possible: there is then least liability for the high-lights to become stained, a defect of most of the toning processes, though less noticeable with catechu than with the others. Wash the prints for a few minutes after toning.

The permanency of prints toned by Roy's process—which the writer considers the most satisfactory of all—may perhaps be regarded by some as somewhat doubtful. Catechu, however, is one of the most permanent dyes, and the tone obtained may be very fairly compared with those of the platinum prints toned by Packham's process. The latter, as the experience of many during the past few years has proved, may be regarded as permanent.

\* *The Photogram*, 1896 (Dec.), p. 299.

*Brown Tone (Tannin process).*—Place the dry prints in—

Liq. ammonia (.880),	6 mins.	12.5 c.cs.
Water, . . . .	1 ounce.	1000 „

As soon as the color has disappeared, rinse for a few minutes and transfer them to—

Tannic acid, . . .	9 grains.	20 grams.
Water, . . . .	1 ounce.	1000 c.cs.

In this solution the prints will gradually assume a brown color. The intensity of the brown deposit is increased by adding a drop or two of the ammonia bath to the tannin solution, but the procedure is apt to cause stained high-lights.

*Purple-brown (Bolle's Tannin and Pyro process).*  
—Make a hot solution of tannic acid and add a trace of pyrogallic acid :—

Tannic acid, . . .	22-35 grains.	50-80 grams.
Pyrogallic acid, . .	Trace.	Trace.
Water, . . . .	1 ounce.	1000 c.cs.

Immerse the print in this for a minute or two until the blue gives way to lilac. Rinse, and place for a moment or two in a caustic potash solution.

Caustic potash, . .	4-9 grains.	10-20 grams.
Water, . . . .	1 ounce.	1000 c.cs.

The process should be conducted as quickly as possible, but a rose-coloured tinge in the high-lights is unavoidable, which, for some subjects, may be an improvement.

*Violet-black (Gallic Acid and Pyro).*—Bolle recommends the following process, with which,

however, the writer has not been successful in obtaining anything but weak and sickly-looking prints. Place in—

Carbonate of soda (cryst.),	22 grains.	50 grams.
Water,	1 ounce.	1000 c.cs.

In this the print changes to pale yellow. Rinse slightly, and place in—

Gallic acid,	4 grains.	8 grams.
Pyrogallie acid,	$\frac{1}{4}$ grain	.5 gram.
Water,	1 ounce.	1000 c.cs.

With gallic acid alone, violet tones are produced, whilst, by increasing the proportion of pyro, a blacker image results.

*Lilac (Bolle's process).*—A lilac color is produced by immersing the print in a hot solution of acetate of lead (sp. gr. 1.24). The prints are then well washed. These lilac prints can be toned still further by placing them in a 35 per cent. solution of potassiumsulphocyanide, pressing between blotting-paper, and drying before a fire : or a better plan is to add a few drops of lead acetate solution to the sulphocyanide, completing the process as just mentioned. The mixed bath of lead and sulphocyanide must be made fresh for each batch of prints.

The color has the obvious disadvantage of not resisting moisture, in the form of perspiration from the hands, damp air, etc. The image, too, fades appreciably in a strong light, and regains its original intensity in the dark. Its most useful application seems to be in toning blue transparencies for lantern slides.



*Black Tones (Lagrange's process).*—Well wash the prints, give a final rinse in *distilled* water, and, in a yellow light, bleach in—

Silver nitrate, . . .	9 grains.	20 grams.
Distilled water, . . .	1 ounce.	1000 c.cs.

Well wash, first in distilled water, fume with ammonia, expose to light, and develop with ferrous oxalate developer.

*Modified Blue.*—

Sulphuric acid, . . .	4 mins.	8 c.cs.
Water, . . . . .	1 ounce.	1000 „

gives a greenish tint to the blue.

Washing with some kinds of tap water reduces the intensity of the blue and at the same time modifies its color. Some hours' immersion gives an exceedingly agreeable blue, particularly for large prints, for which, very often, the ordinary blue is too bright.

According to H. H. Buckwalter,\* the following process gives a very pleasing blue. Place the print in water for a few seconds, then into—

Liq. ammonia ('880), . . .	1 min.	2 c.cs.
Water, . . . . .	1 ounce.	1000 „

in which it bleaches and turns a peculiar purple. When sufficiently reduced, place direct into—

Monsell's salt, . . . .	27 grains.	62 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

for about two minutes. Monsell's salt is basic ferric sulphate. Wash for five minutes on removal from the iron bath.

\* *Canadian Photographic Journal.*

*Brightening the Color.*—The blue color is improved by several baths, applied after washing out the ferricyanide. One is—

Alum,	.	.	.	11 grains.	25 grams.
Water,	.	.	.	1 ounce.	1000 c.cs.

Another—

Oxalic acid,	.	.	.	14 grains.	30 grams.
Water,	.	.	.	1 ounce.	1000 c.cs.

Immerse for about thirty seconds and wash again in water. Citric, nitric, and other acids, potassium bisulphate, bleaching powder, all in weak solution, are among other reagents which answer the same purpose.

*Intensification* to a slight extent is possible by immersion of the prints in a solution of an iron salt, which intensifies probably by combining with ferricyanide occluded by the blue deposit. Immerse in—

Ferric chloride,	.	.	.	2 grains.	5 grams.
Water,	.	.	.	1 ounce.	1000 c.cs.

*Reduction* is a process which is similarly limited in its application. Long washing is the most successful reducer of slightly overprinted proofs. A chemical reducer is :—Immerse in a weak solution of caustic potash till the lines become clear and the ground grey. Then transfer to weak hydrochloric acid till the blue color comes back : then well wash.

Titles, etc., can be written with the oxalate solution given on page 115.

## CHAPTER III

## THE USES OF BLUE PRINTS

COLONEL BADEN-POWELL immortalised ferro-prussiate by issuing one-pound notes produced by that process during the siege of Mafeking. The notes were from 'B.-P.'s' own design. Five hundred of them were issued and not one presented for payment.\*

The simplicity of the ferro-prussiate process will at once suggest many uses for it.

*Trial Prints.*—In the first place, it is eminently suited for making trial prints from negatives. When making the print, a piece of paper, about half an inch longer than the negative, should be used, this additional portion being shielded from light during printing by a piece of opaque paper. The print is thus obtained with a white strip along one edge, on which can be written particulars of the exposure, subject, etc., of the negative.

*Negative Register.*—These prints bound together in lots of twenty-five or fifty make a most useful negative register. The prints are numbered to coincide with the negatives themselves, and it will be found a great convenience to be able to turn up a positive copy of the negative, bearing particulars of exposure, character of negative, etc., instead of looking up the negative itself.

\* *Photography*, 1900, p. 569 (Aug. 30).

*Printing on Tour.*—To the tourist in foreign countries who is anxious to make prints of those negatives which he develops *en route*, the process is to be commended. He may take a supply of paper sealed up, but better a small ruby bottle of sensitising solution and a small sponge. A few minutes' work, after the development of the negatives at night, will place him in possession of the necessary paper on which to print from them the following morning.

*Illustrated Post Cards.*—The same sensitising solution can be called into requisition for producing the indispensable illustrated post card. A sensitising solution which has been specially recommended for this purpose is as follows :—

Ferric am. oxalate, .	30 grains.	70 grams.
Ferric am. citrate, .	30 „	70 „
Water, . . . .	1 ounce.	1000 c.cs.

Sensitise with this solution and develop on—

Potass ferricyanide, .	44 grains.	100 grams.
Water, . . . .	1 ounce.	1000 c.cs.

The Kallitype formula on page 42 is even more suitable for this purpose.

*Transparencies on glass* as well as on paper are within the scope of the process; the latter, particularly, are useful for decorative purposes. For lantern slides and other glass transparencies, glass is cleaned thoroughly and coated with a gelatine mixture :—

Nelson's No. 1 gelatine,	22 grains.	50 grams.
Water, . . . .	1 ounce.	1000 c.cs.

Rinse the gelatine once or twice with water, stand it aside for an hour or so, then dissolve in the water (by warming the two on a water-bath), and filter hot through cotton. Warm the solution to about 130° F., and pour over the plates. Place them on a cold horizontal slab to cool, and, as soon as set, dry, preferably in a drying oven.

Instead of coating plates with gelatine, ordinary lantern plates can be fixed without exposure to light, and well washed; or spoiled lantern plates can sometimes be used for the purpose, after removing the silver image. Farmer's reducer is frequently recommended for this, but is very liable to leave a yellow stain. A better reagent is:—

Sat. sol. of potass cyanide	}	15 mins.	12 c.cs.
in water, . . . .			
Sat. sol. of iodine in	}	5 „	4 „
alcohol, . . . .			
Water, . . . .		3 ounces.	1000 „

after which the plate is well washed.

The plates are immersed for about five minutes in the sensitising solution (page 12), the surface rinsed from sensitiser, and dried in the dark. Printing takes place in the usual manner, except that, unless a special opal transparency frame is used, the process cannot be watched. It is not difficult, however, to form an idea of its progress by looking through the back. Print far deeper than for a paper print, and wash in water as usual.

Collodion has been recommended as a vehicle for

the sensitive iron salts.\* G. Ardaseer gives the following formula :—

Pyroxyline (high temp.),	120 grains.	7·8 grams.
Methylated alcohol (·820),	6 ounces.	170 c.cs.
„ ether,	5 „	140 „

Make this a day or two before using. Allow to settle, and pour off the clear collodion. Edge the plates with indiarubber (in benzole) solution, flow the collodion over, and as soon as set immerse in the sensitising liquid.

Opals, matt or glazed, can be produced by the same methods given above for glass positives, and, given suitable subjects, make very charming ornaments for the shelf or bracket.

*Transparencies on Paper.*—Print very much deeper than for an ordinary print, and, after washing and drying, render translucent by one or other of the well-known methods. One of the simplest is to iron small pieces of paraffin wax into the print with a smooth iron, hot enough to melt the wax. Pieces of best paraffin candle will answer, and the process can be carried out by immersing the print in the melted wax more quickly than by ironing. To do this, get your workroom warm and place the wax to melt in a basin standing in almost boiling water. Warm a zinc tray before the fire, make the print quite dry, and place in the tray. Quickly pour the wax into the tray, and before it sets remove the print. If too much wax is taken up, the print must be warmed before the fire, drained, and

\* *Photography*, 1891, p. 863 (Dec. 31).

pressed between blotting-paper. Castor-oil, as described on page 115, may also be used, but always leaves a very slight greasy feeling.

The trouble of waxing can be avoided by sensitising translucent paper (as used by draughtsmen for tracing) as recommended by Hinsdale Smith,\* who uses a brand of paper known as 'French parchment.' These tracing papers can be obtained in sheets,  $20 \times 30$ ,  $30 \times 40$ , or  $40 \times 60$  inches, from large engineering stations like Gill & Sons, Charterhouse Street, E.C., and can be sensitised like ordinary papers by pinning to a board. The transparencies when finished can be mounted on glass or between two thin cut-out mounts.

*Imitation Tiles.*—The similarity of the color of ferro-prussiate prints to that of the old Delft pictures makes them a fitting medium for preparing imitation tiles, as suggested by Oscar Bolle. Select suitable bold and vigorous subjects, and after the prints are completed, mount on glass or well-seasoned wood. Next, size twice with glue (one part) dissolved in water (10 parts) and varnish with good 'oak' or 'church' varnish.

*Decorative.*—Many little knick-knacks can be ornamented with blue prints made on paper, card, or other material. Bookmarks made from slips of Whatman's rough drawing-paper look very effective when they bear a neatly vignetted landscape, printed in Turnbull's blue.

*For newspaper illustration work* (where the print is to be drawn over for reproduction) a lightly printed

\* *Anthony's International Annual*, 1889-90, p. 218.

blue print answers as well as the bleaching process, used with plain or matt-gelatine paper. The drawing is made with Indian ink and the faint blue image escapes reproduction when the negative is made. The oxalate of potash solution given on page 115 might, of course, be used for bleaching a too deeply impressed print.

*For educational work* in schools and colleges the blue process finds a place. Many lecturers distribute small prints of complicated diagrams, etc., to the members of their class for their future study at home, and when the light permits its use, the simplicity and cheapness of ferro-prussiate recommends it for this work. In dull weather gelatino-bromide must be used, though the uranium process (page 15) is worth a trial. Blue printing has been used in the New York Kindergarten Schools. The children are taught to copy pressed flowers and grasses in the sun and fix the impressions in water.\*

*In the laboratory* the blue print has been found most useful† in recording results of experiments, duplicating notes, etc.

\* *New York Times*, Apr. 11, 1900.

† Chas. H. Himes, Ph.D., *Photographic Times*, 1896, p. 187.



## CHAPTER IV

## FERRO-PRUSSATE IN TRI-COLOR WORK

THE pure blue color given by the ferro-prussiate process has naturally been utilised in recent tri-color work by the superposition method. The tri-color print by W. E. Brewerton medalled at the Royal Photographic Society's exhibition of 1898, had its blue image in ferro-prussiate, and its yellow and red images in transparent inks by the gum-bichromate process. Mr. Brewerton has kindly furnished the writer with particulars of the method employed by him, from which the following is quoted :—

“ Having produced our three good negatives, we first commence to print on ferro-prussiate paper with the negative taken through the red screen. It is very difficult to procure a ferro-prussiate paper which is suitable for the gum-bichromate process. I find a paper sold by Messrs. Marion & Company, in rolls, is the best for the work : it must, of course, be absolutely fresh. Care must be taken not to get the blue print too dark, as this will spoil the finished work. Thoroughly wash in several changes of water, blot on clean white blotting-paper, and immerse in a saturated solution of

potass bichromate (as used by the Autotype Company). Leave in soak three minutes, and hang up to dry in a dark room.

“While the blue print is drying, take half an ounce of ‘Stock solution’ (gum-arabic, 2 ounces; water, 5 ounces, prepared the day before), add half an ounce of water, and stir in the red color, which must be thoroughly ground with a glass muller. The transparent photo colors of Messrs. A. B. Fleming & Company will be found most excellent for the process. Mix some of the ground color with the gum and water, and stir well. The exact proportions of color with gum solution cannot be very well given, as different results require different consistencies, but about one part of color to three parts of gum solution is a fair proportion, which practice will enable the operator to vary according to his requirements.

“Now quickly coat the sensitised surface of the blue print (which has been pinned down to a board) with the mixture, using a hog’s-hair brush: the important point is, get the pigment over the whole surface of the paper very evenly and quickly. Finish off with a soft camel’s or badger’s hair brush. The sensitised paper is then allowed to dry, which takes about half an hour in a warm room—of course, in the dark.

“We now take the negative produced through the green screen and carefully register the print upon it by holding the two up to the light—gas or yellow light will do very well. It may not exactly

register. If too large, slightly warm the print evenly all over. If too small, which is usually the case, pass it rapidly over the top of a jug containing hot water: this will expand the paper to its proper size.

“ When the print and negative coincide exactly, place them in a printing frame and expose to a diffused light for from fifteen to thirty minutes—the precise time can only be found by practice. Having printed the picture, place it in cold water face downwards for two or three minutes, change the water several times, and commence the washing away of the soluble parts. This, I need hardly say to those who have used the gum process, is the most difficult part of the proceedings. Very great care should be taken in manipulating the print, and many methods—running water, sawdust and water, brushes, etc.—can be used to wash away the soluble gum and color. I myself find a piece of cotton-wool the most suitable. A rough print on P.O.P. or ferro-prussiate paper should always be kept in sight, when washing away, as a guide to the removal of the soluble parts.

“ This washing being completed, the double print is then before you (blue and red), and often presents a very pleasing appearance. It now requires the yellow image, which is printed from the negative taken through the blue screen as just described for the red, though I might mention that the yellow requires much less exposure.”

Another tri-color process which may be mentioned

is that of Dr Noack,\* who prints the red image first by a modification of Feer-type. The paper is then re-sensitised with a solution of lead ferricyanide, and a yellow image obtained, after exposure, by treating with potass bichromate solution. Lastly, the blue image is obtained by again sensitising—Valenta's formula (page 14)—followed by exposure and washing in water. There is considerable room for improvement in this process, which, in its present state, presents many practical difficulties.

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## CHAPTER V

### THE KALLITYPE PROCESS

*Theory in Brief.*—Paper coated with a mixture of ferric oxalate and silver nitrate gives, on exposure to light, an image in ferrous oxalate, which, on a suitable solvent of ferrous oxalate being applied, precipitates an image in metallic silver.

This process, which, it will be seen, is on the same lines as Herschel's 'chrysotype,' was patented by W. W. J. Nicol † in 1889, and in the original form in which it was placed upon the market the silver salt was contained in the developer instead of

\* *British Journal of Photography*, 1898, page 822 (Dec. 23), from *Phot. Correspondenz*.

† English patents 5374 (1889), 4269 (1890), 7312 (1891).



PLATE 1. THE GREAT WALL OF CHINA

THE GREAT WALL OF CHINA  
CHINA  
1900

on the paper. The incorporation of the two salts in the sensitive film, as subsequently patented, greatly simplifies the process, which is in fact one of the easiest to work, and affords opportunity for obtaining a variety of tones.

A sensitising solution which gives first-rate results is that of W. K. Burton :—

Ferric oxalate,	. 75 grains.	172 grams.
Silver nitrate,	. 30 „	69 „
Distilled water,	. 1 ounce.	1000 c.cs.

Weigh out the ferric oxalate and place in a stoppered bottle : add the water, place the bottle in a saucepan of water, and gradually raise the temperature, shaking the bottle till the ferric oxalate dissolves. If it does not do so, add a little oxalic acid, say 5 or 10 grains. Any ferrous oxalate contained in the ferric salt is left undissolved, and unless the liquid is quite clear the solution should be passed through a paper filter (page 119). Then add the silver nitrate, and store in the dark. Instead of weighing out the solid oxalate, which is a somewhat expensive salt, the solution of the same, made as described on page 137, can be used, when the above formula will stand thus :—

20 per cent. sol. } ferric oxalate,	410 mins.	852 c.cs.
Silver nitrate,	. 30 grains.	69 grams.
Water to make	. 1 ounce.	1000 c.cs.

A pure paper must be used. Saxe or Rives, Whatman's drawing-papers, and good cartridge-

papers are all suitable. It is found that the paper has considerable influence on the tone. Cartridge-papers give warm sepias with great readiness, but do not yield engraving blacks. Whatman's drawing-papers, on the other hand, do not give a warm brown at all easily.

Coat the paper (pinned to a board) with a tuft of cotton-wool or fine sponge. The writer prefers the latter. Squeeze all surplus sensitiser from the sponge, and draw broad strokes across the paper, afterwards crossing the direction of these to get as uniform a coating as possible. Allow to lie for a minute or so for the solution to sink slightly into the paper. A too superficial coating gives an image which is liable to be rubbed off in the after-treatment. Then dry quickly in front of a clear fire at such distance that the paper does not become appreciably warm to the hands. Overheating will cause fog.

Very rough paper requires greater care in sensitising, to ensure the solution reaching the depressions in the paper. Work in plenty of gas or lamp light, and apply the solution thoroughly by dabbing gently with cotton-wool (W. K. Burton).

Paper will keep some days wrapped in paper, but is best preserved in calcium chloride tubes, in which it will keep for months.

Printing takes place rather more rapidly than P.O.P. The image makes its appearance in the same manner as in the platinotype process, though exposure is complete when a rather less vigorous image of the shadows is produced. Detail at this point



should be faintly visible in the densest portions of the negatives in bluish-brown on the pure yellow ground. Keep the paper dry during printing by backing with oil-cloth or rubber. Damp paper makes it difficult to judge when exposure is correct. If kept dry the paper can be stored for a reasonable time before development.

*Developer for Black Tones.*—

Borax, . . . .	44 grains.	100 grams.
Rochelle salt, .	33 „	75 „
Water, . . . .	1 ounce.	1000 c.cs.
Potass bichromate } sol: (1 per cent.) }	45-55 mins.	94-115 „

The bichromate solution contains :—

Potass bichromate, .	4½ grains.	10 grams.
Water to make .	1 ounce.	1000 c.cs.

Its action is to restrain, and its quantity can be adjusted to suit different types of negatives. Too little bichromate causes muddy prints with stained high-lights ; too much destroys the half-tone.

Immerse the print face up in this solution and remove any air bubbles with the finger or a piece of glass rod. The image attains its full depth in a few seconds, but the prints must be allowed to remain from fifteen minutes (at least) to half an hour, in order to completely dissolve all iron salts in the paper. Neglect of this is the cause of yellow stains in the finished prints. Do not overwork the developing baths, or the vigour and color of the prints will suffer. Ten ounces (300 c.cs.) will develop five to

six dozen half-plates. When not in use, keep the baths in the dark.

Rough-surfaced prints must not be rubbed over each other in the developing or other baths: the friction of one rough surface over another is liable to rub off the silver image, causing a mottled appearance of the print (W. K. Burton).

*Developer for Purple.*—

Borax, . . .	12 grains.	28 grams.
Rochelle salt, . .	44 „	100 „
Water, . . .	1 ounce.	1000 c.cs.
Potass bichromate, { 1 per cent. sol. }	45-55 mins.	94-115 „

*Developer for Sepia.*—

Rochelle salt, . . .	22 grains.	50 grams.
Water, . . .	1 ounce.	1000 c.cs.
Potass bichromate, { 1 per cent. sol. }	25-30 mins.	52-62 „

*Developer for Maroon Tones.*—The following has been recommended :—

Rochelle salt, . . .	44 grains.	100 grams.
Sodium tungstate, .	22 „	50 „
Water, . . .	1 ounce.	1000 c.cs.

*Fixing Solution.*—

Hypo, . . .	1 ounce.	200 grams.
Liq. ammonia (.880),	120 mins.	12 c.cs.
Water, . . .	20 ounces.	1000 „

Hypo was not recommended for fixing in Nicol's original process, but later experience has shown that it is advisable on the score of permanency.

The prints are transferred direct from the developer into this bath, and are turned over frequently for ten minutes; they are then given a similar treatment in a second bath for the same time. Fixing being thus completed, they are washed in running water for about a quarter of an hour and dried.

*Engraving black tones* are obtained by developing with sodium acetate, followed by a solution of potassium oxalate, to render the iron soluble.

*Developer.*—

Sodium acetate, . . .	66 grains.	150 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

*Oxalate Bath.*—

Potass oxalate, . . .	80 grains.	183 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

Wash for a few minutes in several changes, and fix in ammonia solution as before.

Henry Hall \* recommends the following formulæ for Kallitype :—

*Stock solutions for sensitisers.*—

A. Ferric oxalate, . . .	1 ounce.	200 grams.
Distilled water, . . .	5 ounces.	1000 c.cs.
Picked gum arabic, . .	48 grains.	22 grams.
B. Ferric potass oxalate, .	$\frac{1}{2}$ ounce.	62.5 „
Distilled water, . . .	8 ounces.	1000 c.cs.
C. Oxalic acid, . . . .	$\frac{1}{2}$ ounce.	125 grams.
Distilled water, . . .	4 ounces.	1000 c.cs.
Ammonia (·880), . . .	100 minims.	50 „
D. Potass bichromate, .	120 grains.	70 grams.
Distilled water, . . .	4 ounces.	1000 c.cs.

\* *The Photo-Miniature*, No. 47.

For average negatives mix A, 1 oz. ; B,  $\frac{1}{2}$  oz. ; C, 30 minims ; D, 4 drops. The sensitiser is made from this mixture by adding 6 grains of silver nitrate to 120 minims of it. For contrasty negatives, omit D and increase B and C, the latter by not more than 20 per cent. (*i.e.* to 36 minims), or fogging is apt to result. B can be doubled without ill effect, and if this is done another grain of silver nitrate should be added.

For very thin and soft negatives increase D—to double in bad cases, at the same time reducing C by one half or more.

*Developer.*—Sodium acetate solution (1 in  $7\frac{1}{2}$  of water) 8 ounces (1000 c.cs.) ; tartaric acid, 12 grains (3·1 grams) ; solution D, 10 to 100 minims (2·5 to 25 c.cs.).

*Clearing Bath* for acetate developed prints :—

Sodium citrate, . . .	$\frac{1}{4}$ ounce.	31 grams.
Citric acid, . . .	20 grains.	5·5 „
Water, . . .	8 ounces.	1000 c.cs.

If the borax and Rochelle salt developer is used the following clearing bath is used :—

Rochelle salt, . . .	$2\frac{1}{2}$ ounces.	80 grams.
Rain water, . . .	32 „	1000 c.cs.
Solution D (bichromate),	$\frac{1}{4}$ ounce.	8 grams.

The prints are treated in these clearing baths for thirty minutes.

The prints are thoroughly washed after the clearing bath—the function of which is to render the iron

salts thus removable by the water—and then fixed for ten minutes in :—

Hypo,	. . .	1 ounce.	50 grams.
Water,	. . .	20 ounces.	1000 c.cs.
Ammonia ('880),	. . .	120 minims.	12 „

*Print-out Kallitype* was patented by Nicol (potass oxalate being included in the sensitising solution), but has not been at all used. Brooke\* has given formulæ and directions.

*Reducing Kallitypes.*—As the image is a silver one, Kallitypes are amenable to the ordinary 'reducer.' Hall,† however, prefers a weak solution of hydrobromic acid (35 minims of the strong commercial acid in 1 ounce of water). It is kept moving for a minute or two over the print, which is then given several quick changes of water and dried.

For correcting prints lacking in pluck the hydrobromic acid solution is applied for a short time, the prints rinsed, fixed in hypo solution for five minutes, and washed and dried.

*After-treatment of Kallitypes.*—The prints can be bleached in—

Hydrochloric acid {	10 mins.	20 c.cs.
(sp. gr. 1·2), }		
Water, . . .	1 ounce.	1000 „

well washed, exposed to light, and developed with metol or other developer. Strong developer gives

\* *Photography*, 1895, p. 778 (Dec. 5).

† *The Photo-Miniature*, No. 47.

black tones ; a weak one, warm tones (red-brown, etc.), which can be further changed to purple in a sulphocyanide toning bath, single or combined.

The original warm-toned Kallitypes can be toned in gold baths, of which that recommended by Dr. Frederick \* is the most noteworthy :—Water, 8 ounces ; hypo, 1 ounce ; gold chloride, 1 grain.

For toning with platinum use the following bath :—

Potass chloroplatinite,	$\frac{3}{4}$ grain.	1.7 grams.
Citric acid, . . . .	$\frac{1}{4}$ „	.6 „
Water, . . . . .	1 ounce.	1000 c.cs.

Uranium toning can also be applied successfully to Kallotype prints, if due care be taken to thoroughly remove all soluble iron salts.

These after-processes, however, are not of much importance. The chief claims of Kallotype are the ease and directness with which it gives prints in metallic silver free from gelatine or other vehicle.

A modification of Kallotype is used considerably on the Continent ; although the results do not at all approach those by the methods already given, the process is more akin to the 'Sepia' paper described in another chapter. Under various fancy names it appears on the market—as 'Simili-platinum' and other papers, and as single sensitising solutions. The following formulæ for a paper and a sensitiser are as good as any.

To prepare the paper, first make the following stock solutions :—

\* *The Photo-Miniature*, No. 47.

A. Green ferric ammo-	}	110 grains.	2.5 grams.
nium citrate, .			
Water, . . . .		1 ounce.	1000 c.cs.
B. Tartaric acid, . . .		18 grains.	4 grams.
Water, . . . .		1 ounce.	100 c.cs.
C. Silver nitrate, . . .		45 grains.	10 grams.
Water, . . . .		1 ounce.	100 c.cs.
D. Gelatine, . . . .		30 grains.	7 grams.
Water, . . . .		1 ounce.	100 c.cs.

Distilled water is best used throughout, but certainly for C. A and C will keep for months in the dark ; B for a week or so only, unless a little carbolic acid is added, but it is better to use it without this addition. The gelatine solution should be made at the time of use. The gelatine is first allowed to swell in a portion of the water for half an hour, and is then dissolved by adding the remainder and placing the vessel containing the whole mixture in a pot of boiling water.

To compound the sensitising mixture we mix equal parts of these four solutions (say, 1 dram each) as follows :—If the gelatine solution has set, place it in warm water until fluid, pour out into a shallow cup, likewise standing in warm water. Now add A and B, and lastly—a few drops at a time and stirring all the time with a bit of glass rod—the silver nitrate solution C. The mixture is kept lukewarm and mopped all over the paper, which is laid on a bit of board a little smaller than itself. There is then no margin of board from which dirt can be picked up during coating. Use a piece of cotton-wool to apply the liquid, dabbing the solution quickly all over, and at once proceeding to even up the coating with a flat

camel's-hair brush, go over the surface lightly, first one way across the paper and then the other. The brush should not be pressed or rubbed on the paper, but just dragged to and fro, holding it loosely between the thumb and finger. As soon as the coating begins to look dull or matt, hang up to dry. In summer, paper should dry in a few minutes, but in winter it is well to place it some feet from a fire, not near enough, of course, to scorch it. Both sensitising and drying should be done in a dim light. A room by gaslight, or rather darker than as used for toning P.O.P., is a safe place.

The negative is printed until a fairly vigorous image is obtained in which the details in the highlights of the original begin to be apparent. The print is developed by placing in plain water for about two minutes, in which it takes on a reddish-brown color. It is then transferred to a solution of sodium thio-sulphate (hypo) for a minute or two—hypo, 10 grains ; water, 1 ounce (20 grams per litre).

Here the print becomes brown in color and loses slightly in density. If allowed to remain too long, or if too strong hypo is used, the loss in density becomes appreciable. Washing for an hour or so completes the process. The method does not render fine gradations well : it requires a fairly strong negative.

The single solution sensitiser is made as follows :—Dissolve 55 grains (3·5 grams) of silver nitrate in 4 to 5 drams (about 15 c.cs.) of distilled water, and add ammonia drop by drop until the white precipitate first formed is redissolved. Now add, drop by drop,



dilute sulphuric acid with constant stirring until the odour of the ammonia almost entirely disappears. Forty grains (2·6 grams) of green ferric ammonium citrate are now dissolved in 6 drams (20 c.cs.) of water and mixed with the silver solution. This liquid keeps well in a stoppered bottle in the dark. A tin canister is a convenient case in which to store the bottle containing it. Brush over the paper as already described, print as before, and fix in the following bath :—

Hypo, . . .	100–150 grains.	30–45 grams.
Soda sulphite, . .	30–100 „	10–30 „
Water, . . .	7 ounces.	1000 c.cs.

The exact strength does not matter : it is near enough if it falls between the two quantities named in the formula.

*Kallitype for Newspaper Work.*—Kallitype prints have been used for preparing drawings for process reproduction. A print is taken in sunlight or by the electric arc, developed, fixed, washed, pasted on a sheet of glass, and dried. The lines are put in with waterproof Indian ink and the print bleached with bichloride of mercury. When finished with, the print is removed from the glass by soaking in water.

*Permanency of Kallitype.*—The fact that the chemical *rationale* of Kallitype printing favours the conclusion that the image is metallic silver has been assumed by some writers as sufficient guarantee of its permanency. It should, however, be borne in mind that when in a finely-divided condition silver,

like platinum, is apt to carry down certain compounds of iron, to which very often the color of the deposited metal is due. The criticisms passed on Carey Lea's work on the so-called allotropic forms of silver will call to mind this characteristic property of the finely-divided metal. In the case of platinum prints no reaction between the iron and the platinum need be feared, but silver is a metal more susceptible to chemical change, and it is possible that it may undergo gradual oxidation by traces of associated ferric salt. There is no doubt that numbers of Kallotype prints have stood the test of time for six years or more, whilst others have faded.

Hence the task of obtaining permanent prints resolves itself into the complete removal of iron salts from the paper, and attention is therefore best directed to the proper sizing of the paper, with a view to prevent the iron salt attaching itself to the fibre of the paper, and to a thorough treatment with alkaline and neutral solvents of iron salts. Experience shows that an ammonia fixing bath is not sufficient to guarantee permanency, and the hypo bath, preceded by the thorough removal of the iron salts, should be adopted from the practice of Hall and other later workers of the process. Toning with gold or platinum may, of course, be done, but the simplicity and cheapness of Kallotype is at once discounted, and one might as well use platinotype right away.

## CHAPTER VI

## THE OBERNETTER PROCESS

*Theory in Brief.*—Paper is coated with a mixture of ferric and cupric chlorides. The former of these is reduced on exposure to light to ferrous chloride. In the presence of moisture the ferrous chloride reduces the copper salt to cuprous chloride ( $\text{Cu}_2\text{Cl}_2$ ). On immersion in potassium sulphocyanide solution, cuprous sulphocyanide (white) takes the place of the cuprous chloride. After washing out the excess of salts, the white image is developed with potassium ferricyanide or other reagents.

This process, which takes its name from its inventor, J. B. Obernetter, was published in 1864, and gives quite easily a variety of tones which there is very good reason to regard as permanent.

Obernetter's original formula for coating the paper is :—

Copper chloride,	. . . . .	100 parts.
Ferric chloride sol. (sp. gr. 1.5),	13	„
Hydrochloric acid,	. . . . .	12 „
Water,	. . . . .	1000 „

The writer prefers to increase the proportion of ferric chloride in the above formula. A paper is

thereby obtained which gives a more visible image and yields prints of greater vigour.

A suitable proportion is 30 grams of anhydrous ferric chloride (46 c.cs. of B.P.\* sol., sp. gr. 1·42). The modified formula is as follows :—

Ferric chloride (B.P. sol., sp. gr. 1·42),	} 22 mins.	46 c.cs.
Copper chloride,	44 grains.	100 grams.
Hydrochloric acid,	5 mins.	10 c.cs.
Water,	1 ounce.	1000 „

A strong paper, such as Steinbach ferro-prussiate, should be used and should be well sized. A solution of gum-arabic (10 grains per ounce or 23 grams per litre) brushed over, answers well. The paper is floated for two minutes on the above solution and dried in artificial light. The paper, which is not so sensitive as albumen paper, keeps very well indeed before exposure. It is printed until a very faint image appears, it being rather more difficult to judge the right point than in platinotype printing. Development must follow exposure as soon as possible, within two hours at the latest. If longer than this elapses, the cuprous chloride gradually reverts to the state of higher oxidation, and after twenty-four hours the paper can be exposed afresh.

The developer contains :—

Potass sulphocyanide,	5 grains.	12 grams.
Sulphuric acid (conc.),	$\frac{1}{4}$ min.	·5 c.cs.
Sensitising solution,	5-6 mins.	10-12 „
Water,	1 ounce.	1000 „

\* B.P. = *British Pharmacopæia*.

This forms a deep red solution which deposits a small precipitate after standing some time. This may be neglected and the clear solution decanted for use. The developer can be used over and over again.

Float the paper for three or four minutes, face down, then gently immerse : float the next, agitating the liquid as little as possible during these operations. The prints may be immersed for from five minutes to half an hour. When all have been treated, transfer to a dish of clean water and wash in running water for an hour. A very faint image is visible on removal from the sulphocyanide bath, but this almost entirely disappears on washing. At this stage of the process the prints may be dried and put away until convenient to make the image visible by the action of the next bath.

Potass ferricyanide, .	44 grains.	100 grams.
Water, . . . .	1 ounce.	1000 c.cs.

This solution gives a red or terra-cotta colored print. It acts only slowly, but the prints require no attention. An immersion of several hours does no harm, and is, in fact, generally necessary. When the desired tone and intensity is reached, wash in running water for a quarter of an hour or so, and dry.

The red prints, thus produced by ferricyanide, can be further toned through a series of tints by immersion in an acid-iron solution. To insure the success of the toning process, the prints must be

thoroughly washed free from ferricyanide, or blue stains result. The toning solution is :—

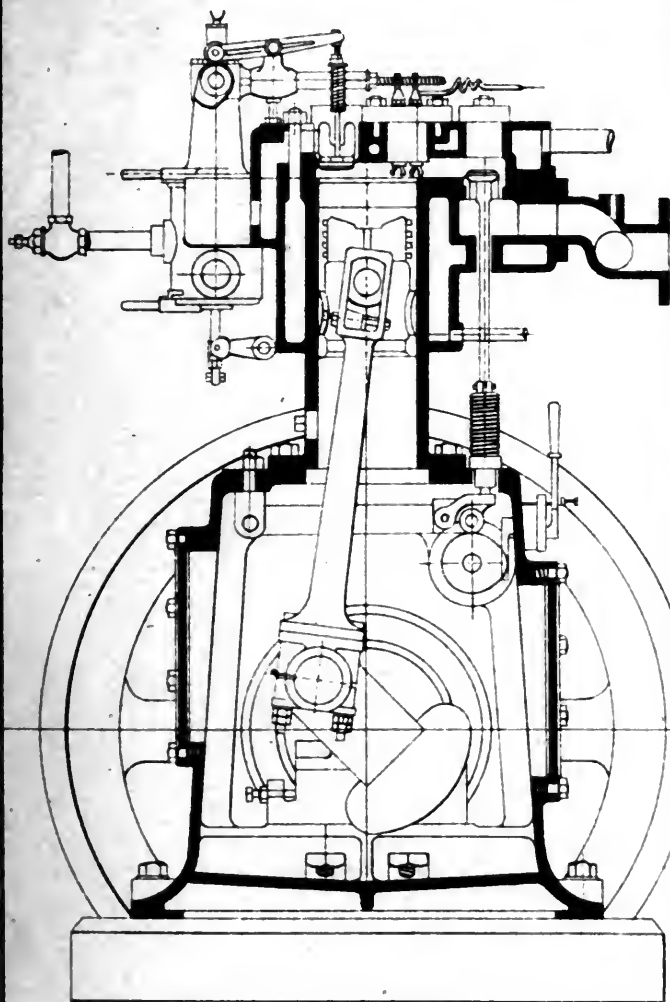
Ferric chloride (cryst.),	57 grains.	130 grams.
Ferrous sulphate,	. 145    "	330    "
Hydrochloric acid,	. 123    "	280    "
Water,	. . . . . 1 ounce.	1000 c.cs.

In this bath the red tone gradually passes through reddish-violet, blue-violet, and black to greenish-black. The prints are then washed in one or two changes of water, acidulated with hydrochloric acid, then in plain water, and dried. It need hardly be said that the greatest care must be exercised in keeping the last quoted solution and the ferricyanide separate. Traces of one carried into the other on fingers or prints will produce blue stains wholesale. The strongly acid character of the toning bath necessitates a stout paper and careful handling.

A purple-violet tone resembling a silver print is produced by washing the prints for a minute or two from the iron solution and placing them for a few seconds in a very weak solution of acetate of lead.

Other tones can be obtained (after washing out the ruddy developer or sulphocyanide of iron) by silver nitrate and by permanganate of potash. The former is used in weak (2 per cent.) solution and gives a cold black image, the print being afterwards fixed in water containing a little oxalate of ammonium. The exposure, for development with silver nitrate, must be much shorter; the exact point is rather difficult to hit.

*Black Line Copy. Water Bath Development.*



*"Perfection" Brand Paper.  
Bemrose & Sons, Ltd. Derby, Leeds & London.*





Potassium permanganate is dissolved in water and a few drops of ammonia added. The strength of the mixture is not very important, and the bath gives brown tones. The writer's experience is that the ferricyanide and iron toning baths are preferable to either of the two last named.

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## CHAPTER VII

### THE URANOTYPE PROCESS

*Theory in Brief.*—Uranic salts exposed to light yield uranous salt, which gives, with potassic ferricyanide, a red image of uranous ferricyanide.

The use of uranium salts for printing dates back to the very early days of photography, but uranium processes have never come into extended use. A uranium paper was formerly on the market, but at present, so far as the writer knows, no paper of this kind is commercially obtainable.

The ordinary uranium process is, however, very simple, and easily gives certain colored images. The sensitising solution is :—

Uranium nitrate,	88 grains.	200 grams.
Water to make,	1 ounce.	1000 c.cs.

Paper is floated on this solution for about five minutes, and dried before the fire as quickly as

possible. The pale lemon-colored paper must be kept quite dry by storage in a calcium tube.

Uranotype requires a vigorous, even hard, negative. It is useless to expect good results from a thin, flat negative, and printing should be carried out in sunlight to get the best results. The uranium image—purplish-brown—is much more visible than that obtained with Kallotype or platinotype, and it is quite easy to judge when exposure is complete. The exposed paper, however, possesses the peculiarity of gradually losing its image when kept in the dark, so that it is obvious that development must follow exposure fairly soon, and that over-exposure can be readily corrected.

*Preliminary Washing.*—Before development with ferricyanide, the paper is washed for ten minutes or so in several changes of water. Those who have used uranium for toning bromide prints will know that the use of a current of water for washing is liable to give rise to patchy prints, and that therefore moving the prints in a dish of still water is preferable to more energetic treatment in a print washer. This washing being completed, the print is ready for development.

*Developer.*—

Potass ferricyanide,	55 grains.	125 grams.
Water, . . . .	1 ounce.	1000 c.cs.

The prints can be immersed in this developer, or it can be applied with a camel-hair mop or tuft of cotton-wool. The print develops in a few seconds to a clear Bartolozzi red.

*Final Washing.*—Ten minutes' washing in several changes of water completes the process, so far as the red print is concerned.

*Toning the Red Print.*—The red uranium image is amenable to considerable treatment with iron and cobalt salts, and yields, according to the precise process adopted, prints in sepia, green, or blue.

*Sepia and Green.*—

Cobalt nitrate,	. 30 grains.	69 grams.
Ferrous sulphate,	. 90 „	206 „
Water, . . .	. 1 ounce.	1000 c.cs.

In this solution the washed red print rapidly passes from red, through sepia, to green. To obtain intermediate colors it is necessary to remove the print at once and to plunge it into a large dish of water. Then it is washed for a minute or two, changing once or twice, pressed between blotting-paper, and dried before the fire.

Another bath recommended for green tones is :—

Cobalt nitrate,	. 1½ grains.	3 grams.
Ferrous sulphate,	. 3 „	7 „
Citric acid, . .	. 12 „	28 „
Water, . . .	. 1 ounce.	1000 c.cs.

in which the prints are allowed to remain all night.

*Blue Prints.*—Immerse in—

Ferrous sulphate,	. 100 grains.	230 grams.
Nitric acid, . .	. 8 mins.	17 c.cs.
Water, . . .	. 10 ounces.	1000 „

*Fixing.*—Prints which have been toned in either of

the three foregoing baths must be afterwards passed into a fixing bath of—

Citric acid, . . .	44 grains.	100 grams.
Water, . . .	1 ounce.	1000 c.cs.

where they remain for ten minutes. Twenty minutes' washing in several changes completes the process.

*Purple Tones.*—Instead of developing with ferricyanide, chloride of gold can be used to produce an image of metallic gold. The prints must be deeply printed, washed as usual, and developed in—

Gold chloride, . . .	4 grains.	·25 grams.
Water, . . .	1 ounce.	30 c.cs.

This is followed by several minutes' washing.

Local development with ferricyanide solution can be carried out just as in platinotype by thickening the solution with glycerine.

## CHAPTER VIII

## PRINTS ON FABRICS—PRINTS IN DYES

SILK, Nainsook muslin, fine linen and cotton fabrics can each be used as a support for the sensitive coating, and, besides offering facilities for pictorial effect in large sizes, make it possible to turn out decorative articles of domestic use such as d'oyleys, mats, anti-macassars.

The fabrics should be as pure as possible. Many low grades of silk are so weighted with mineral matter as to make them quite unsuitable. Purchase a fine quality silk and wash thoroughly in hot water; allow to very nearly dry, and iron flat.

The fabric must be well sized to keep the image on the surface. Arrowroot is one of the best sizes. Immerse the fabric in a thin gelatinous solution of arrowroot for a few minutes, pin down to a board, and dry before the fire. The fabric should be slightly stiff after drying. An arrowroot and gelatine size is recommended by E. A. Robins.\*

Arrowroot,	.	.	50 grains.	10 grams.
Nelson's gelatine,	.	.	18 „	3 „
Alum,	.	.	11 „	2 „
Water,	.	.	12 ounces.	1000 c.cs.

\* *The Photogram*, 1897 (June), p. 171.

The sensitising solution (ferro-prussiate, Kallitype, etc.) is brushed over, and the fabric dried as quickly as possible. For effective prints the negative should be broad in subject, of vigorous density, and without a superabundance of detail. Often negatives which have been discarded as too hard for paper printing will be found to possess the characteristics requisite for decorative work on fabrics. If they are to be made specially, photo-mechanical or lantern plates should be used and development adjusted to get contrasty negatives.

Ferro-prussiate prints on fabrics will not withstand washing in soap and water, as the free alkali destroys the blue image. A process for replacing the blue image by various adjective dyes has been developed by Stewart E. Carter.\*

Bleached cotton or linen fabric is brushed over with a ferro-prussiate sensitizer made as follows :—

Ferric am. citrate, .	164 grains.	375 grams.
Water, . . . .	1 ounce.	1000 c.cs.
Potass ferricyanide, .	164 grains.	375 grams.
Water, . . . .	1 ounce.	1000 c.cs.

Use equal parts. Expose and wash as usual. The blue print is next immersed in a weak solution of caustic soda.

Caustic soda sol. (sp. } gr. 1.35), . . . .	1-2 mins.	2-5 c.cs.
Water, . . . .	10 ounces.	1000 ,,

\* *Journ. Soc. Chem. Indus.*, 1898 (May), p. 436, and *British Journal of Photography*, July 7, 1898.

The strength of this solution is approximately—

Caustic soda,	.	.	5 grains.	1.1 grams.
Water,	.	.	10 ounces.	1000 c.cs.

It is next well washed in hot water and placed in—

Sodium hyd. phosphate,		13 grains.	3 grams.
Water,	.	10 ounces.	1000 c.cs.

for three minutes at a temperature of 170° Fahr. This is followed by washing first in cold and then in hot (160° Fahr.) water, after which the print is ready to receive the dye.

A weak gelatine solution is made :—

Glue size,	.	.	24 mins.	5 c.cs.
Water,	.	.	10 ounces.	1000 „

This is heated to 160° Fahr. and the prints moved about in it for two or three minutes ; from three to five grams per litre (1.3 to 2.2 grains per ounce) of dinitroresorcine (resorcine green) is added, and the temperature raised to 180° Fahr. As soon as the shade is considered full enough for a strong picture, remove to boiling water, to wash out all unfixed dye. The whites are next cleared in a bath of neutral soap (used at 160° Fahr.) and the print again washed in hot water and finally in cold. Other dyes besides resorcine green can be used. Galloeyanine gives violet and blue ; alizarin gives purple ; alizarin brown, sepia. A somewhat similar process has been patented by A. F. Hargreaves (Eng. Patent, 25,043, 1898). The blue iron compound is said to behave like oxide of iron as a mordant. The blue prints

are therefore subjected to the action of a dye bath containing madder, alizarin, purpurin or logwood. The bath is first used at 100° Fahr., and is raised during thirty to forty minutes, to boiling, then agitated the whole time. The prints are then well washed, treated to a boiling solution of soap, again washed, dried and pressed.

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## CHAPTER IX

### HELIOGRAPHIC PROCESSES COMPARED

SOME idea of the use made of heliographic copies of tracings by engineers, architects, surveyors and others may be gathered from the estimate of the Wm. Cramp & Sons Ship and Engine Building Co., that 11,000 square feet of blue paper are used in the building of a battleship.

Who introduced the iron copying processes to engineers, the writer does not know. In America Thomas H. M'Collin has been credited with doing so in 1871.\*

It should be noticed that the terms positive and negative, as applied to these processes, are held by engineers to have meanings as follows:—A 'positive' paper is one which gives, for an ordinary line tracing, a copy in dark lines on a white ground; a 'negative'

\* *American Journal of Photography*, 1894, p. 481 (Nov.).



paper is one which gives, under similar circumstances, a copy in white lines on a dark ground.

For large work the chief processes are four in number :—

<i>Process.</i>	<i>Copy from line tracing.</i>
Ferro-prussiate.	White lines on blue ground.
Pellet.	Blue    "    "    white    "
Ferro-gallic.	Black   "   "   "   "
Brown.	White   "   "   brown   "

*Ferro-prussiate* is the simplest and cheapest of these. It requires only the slightest experience to work it successfully, and necessitates the smallest outlay in the way of baths and space. Formerly its slowness in printing was one of its chief disadvantages, but paper is now obtainable which almost rivals 'Pellet' paper in rapidity. Its blue ground is the chief objection which draughtsmen urge against it, though the writer has often heard mechanics and others (who use blue prints in the shops) say that they prefer them to the white ground copies.

'*Pellet*' paper is known by various other names, such as 'Cyanifer,' 'Positive Ferrottype,' 'Cyanographic,' etc. It is certainly the most rapid paper, and for winter work especially valuable. It requires greater skill and experience to work it, and a series (four) of baths for development and subsequent treatment.

*Ferro-gallic* paper is much less sensitive than 'Pellet,' but scores over the latter in its simplicity of after-treatment, requiring only one chemical bath,

or, in the case of the 'water-developing' paper, merely washing in water. The black line is said to be preferred to the blue of the Pellet paper as giving a more truthful copy of the tracing, a preference which is purely a matter of taste and should be put alongside the fact that the ferro-gallic process rarely gives the absolutely white ground which 'Pellet' paper does, a faint violet tinge being almost always unavoidable.

The '*brown*' or '*sepia*' is a process which is coming into favour on account of its rapidity, simplicity, and particularly, because of its adaptability to turning out a number of positive copies (brown line on white ground) from a negative intermediate (white line on brown ground), printed directly from the tracing (page 102).

Other processes which are used to a much smaller extent, and chiefly for fine work, are described in Chapter XVII. Platinotype (which is not there described) is also used, and gives very perfect copies. Unfortunately its expense and the precautions needed in its use preclude its general adoption, though it has been used to a fair extent for the reproduction of reduced copies of drawings. The Locomotive Department of the L. & N.-W. Railway Co. is a case in point.

Which of these processes shall be adopted by a drawing office setting up a heliographic outfit is a question upon which it is not easy to give advice. For occasional prints, such as an architect or surveyor is likely to require, the ferro-prussiate or ferro-gallic is best suited. For the regular routine

of a factory, where a large number of prints are wanted every day and often urgently, the 'Pellet' process should certainly be installed. At any rate, the foregoing few hints will help the reader to decide for himself.

## CHAPTER X

### PREPARATION OF HELIOGRAPHIC PAPERS

#### *Ferro-prussiate—Pellet—Ferro-gallic—Brown-line*

*Ferro-prussiate.*—Although few printing houses will wish to themselves prepare Pellet and ferro-gallic papers, the coating of ferro-prussiate paper demands so much less skill than either of these processes that many printers may very well prepare it for their own use. Apart from the question of diminished cost, the superior results, consequent on the employment of fresh paper, will make the procedure worth while.

For a satisfactory and rapid printing paper the writer recommends the formula given on page 14, which is here repeated :—

Ferric am. citrate (green),	110 grains.	250 grams.
Water, . . . . .	1 ounce.	1000 c.cs.
Potass ferricyanide, . . . . .	40 grains.	90 grams.
Water, . . . . .	1 ounce.	1000 c.cs.

Mix equal volumes. This keeps well in the dark, beyond requiring to be filtered just before use, and prints very rapidly.

An equally good though slower formula is :—

A. Ferric am. citrate,	}	1 ounce. 113 grains. 260 grams.
Water,	.	4½ ounces 1 ounce. 1000 c.cs.
B. Potass ferri-cyanide,	}	5 ounces. 75 grains. 172 grams.
Water,	.	32 „ 1 ounce. 1000 c.cs.

Mix equal parts (Lietze).

A standard formula is that of Fisch.\*

Tartaric acid,	.	3 ounces. 153 grains. 95 grams.
Water,	.	13 „ 90 mins. 375 c.cs.
Ferric chloride sol. (sp. gr. 1.45),	}	2 „ 390 „ 80 „
Liq. ammonia (·880), not more than	}	6 „ 70 „ 175 „
Potass ferri-cyanide,	{	2 ounces (av.), — 2 „ 360 grains. 70-80 grams. 205 grs.
Water,	.	9 „ 325 min. 270 c.cs.

Dissolve the tartaric acid in the water, add the iron solution, and then the ammonia, with constant shaking till neutral. Add now the ferricyanide solution with constant shaking, cool, and keep in well-corked bottles in the dark.

It would be easy to multiply formulæ, but one or two from authoritative sources may be given.

\* *La Photocopie*, p. 32, Paris, 1890.

C. B. Talbot \* gives :—

Potass ferricyanide, .	53 grains.	122 grams.
Liq. ammonia (.880), .	4 mins.	8 c.cs.
Ferric am. citrate, .	86 grains.	197 grams.
Distilled water, .	1 ounce.	1000 c.cs.

Dissolve the ferricyanide in the water, let stand a few hours, add the ammonia and then the dry flakes of ferric am. citrate, stirring these in with a glass rod. One fluid ounce coats  $1\frac{1}{2}$  square yards of paper ; 100 c.cs. coat  $4\frac{1}{2}$  square metres.

Another very sensitive sensitiser is :—

Ferric chloride (cryst.),	175 grains.	400 grams.
Oxalic acid, . . .	44 „	100 „
Water, . . .	1 ounce.	1000 c.cs.
Potass ferricyanide, .	88 grains.	200 grams.
Water, . . .	1 ounce.	1000 c.cs.

Mix the two solutions. The coated paper keeps only a very short time.

The rolls of paper are sensitised on a table about half an inch narrower than the width of the roll.

A roller at one end of the table delivers the paper as required, and a drying frame at the other end serves to receive the coated paper in serpentine folds for drying. The top of the drying frame is provided with six or eight detachable rods, which are slipped underneath the paper as each table-length comes from the coater's hands, and placed in slots provided for them in the frame (fig. 1). By enclosing the drying frame in a closet, in the lower part of which a coil of

\* *The International Annual*, 1889-90, p. 233. Anthony & Co., New York,

steam or hot-water pipes is fixed, the paper is quickly dried (C. B. Talbot).

Coating should be done with a fine sponge, taking off any surplus sensitiser with a second sponge, only just moist with sensitiser. The dry coated paper should be of a greenish-yellow color, and must be kept as dry as possible in a moderately warm place. Damp is fatal to its keeping properties.

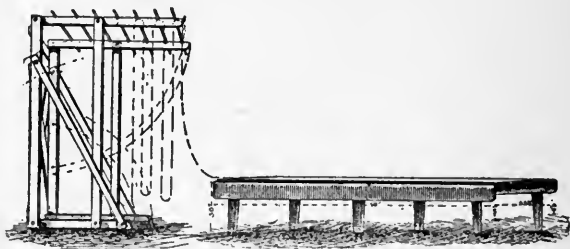


FIG. 1.—Coating and Drying Paper.

For coating by machinery two types of machine are used. The following account of their construction is from a paper by Alfred L. Cohn\* :—

“In fig. 2 is shown a machine used chiefly on the Continent. In this the framework is of iron. The roll of paper, *a*, to be sensitised, is placed on its bearings, and the paper led over an arc-shaped sheet of zinc, *b*, to afford the necessary friction and keep the paper smooth; it then passes under the roller *c* and over *d*. From this the paper is taken up and carried over an endless felt belt, stretched over the rollers *e* and *t*, whence it passes through a narrow

\* *Journal Soc. Chem. Indus.*, 1902, p. 582.

slit into a long closed chamber 10 to 20 feet in length, wherein it is dried, and on its issuing is led back to the machine, where it is wound up on the roller *g*. The bottom of the drying chamber is made of sheet iron, and is heated by Bunsen burners, or coils of steam pipe are laid inside the chamber. The vapour-charged air within the chamber is removed by means of an exhaust fan or blower.

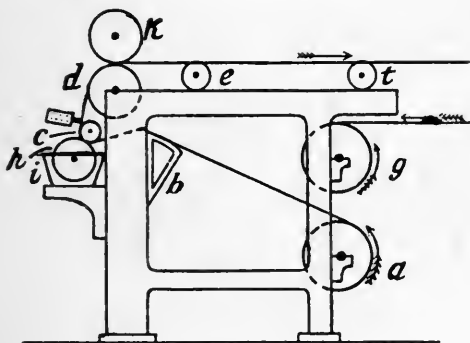


FIG. 2.

*a*, roll of paper; *b*, guide to sensitising rollers *c* and *h*; *d*, guide roller (sensitised paper); *g*, collecting roller. Glass scraper between *c* and *d*.

“The paper, whilst passing around the roller *c*, becomes charged with the sensitising solution which is applied by the roller *h*. This roller is made to revolve *towards* the paper, and dips into the sensitising solution contained in the trough *i*. At a convenient place between the rollers *c* and *d* is fastened the scraper, a sheet of glass, one edge of which is bevelled, and which is held in a frame pivoted to the iron frame of the machine. The

scraper may be applied against the paper with more or less pressure, and at the angle best suited for securing the best results. In some machines, wheels, *k*, with rubber tyres, are placed at each end of the roller *d*, and are operated so as to draw the paper along at its edges until it has been taken up by the roller *g*, when the wheels are lifted from the paper. Of course, the paper will show where these wheels passed over it.

“The machine shown in fig. 3 is constructed of

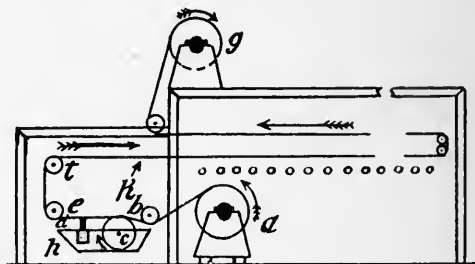


FIG. 3.

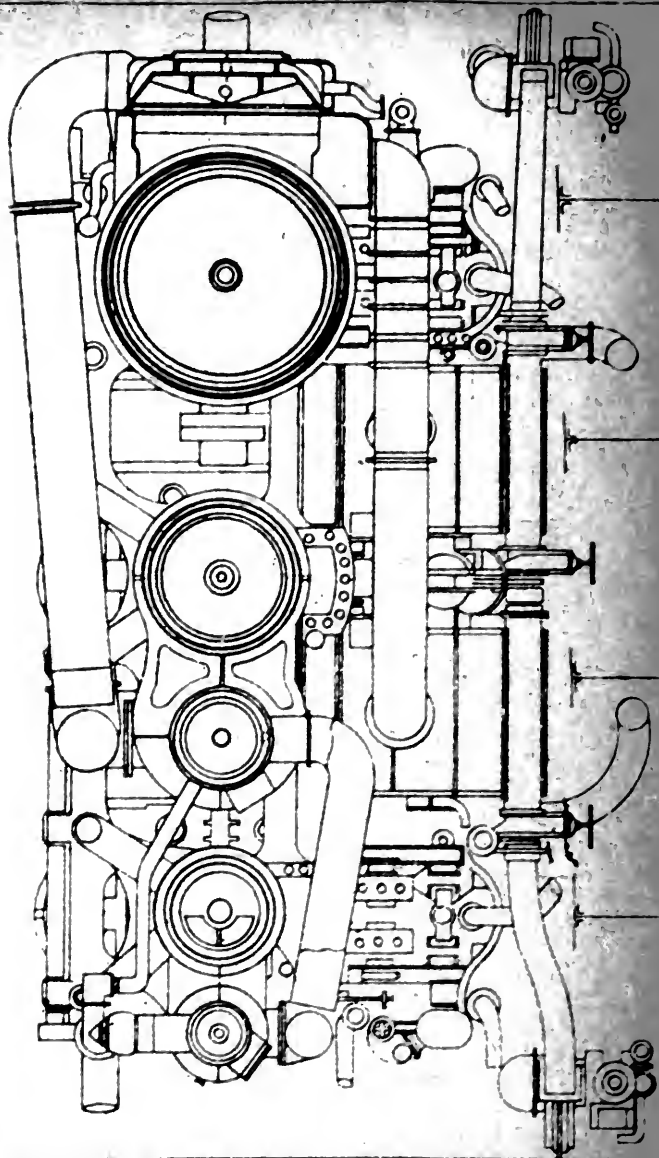
*c*, sensitising roller ; *d*, glass scraper ; *e* and *t*, guide rollers ;  
*g*, collecting roller.

wood. The writer has operated both kinds of machines, and prefers the latter, which he considers much the better of the two. In this machine the roll of paper is borne by a carrier sliding in grooves or on rails. The paper is first passed under a tension roller, is then sensitised by the roller *c*, the excess of liquid being scraped off by the glass scraper placed at *d* ; it next passes over the rollers *e* and *t* to the end of the machine (which may be 20 or 30 feet long, or any convenient length), where it





Copy on Gotz's Ferro Gallic Paper by Development



From Marine Engineer.

passes over two rollers and returns to be wound up on the roller *g*. The paper in its passage through the length of the machine is supported by a criss-cross of string stretched from side to side, in order to prevent too much sagging, and yet allow the paper to be thoroughly dried by the coil of steam pipes placed beneath it.

"The rolls of paper as ordinarily received are of varying widths, 30, 36, 42, 48, etc., inches, and contain usually several hundred yards. The paper is wound on a wooden cylinder, with a hole, either square or round, running lengthwise through it. The roll of paper is supported in its carrier by thrusting through the hole in the wooden cylinder a long iron rod each end of which is threaded, but in contrary directions.

"After the rod is in place a tapering nut with hexagonal or octagonal head, fig. 4, is screwed down on each end. The conical parts of the nuts enter the holes in the ends of the wooden cylinder, and on being screwed up tight the roll is centred and held firmly. The rod bearing the roll is now placed in the bearings of the carrier. The rod is threaded oppositely at the ends, because otherwise one of the nuts would invariably become loose by revolving in the direction in which the paper is pulled. As it is, it is safest to always use an additional ordinary nut, which is screwed down on each conical nut when the latter has been firmly fixed in place.



FIG. 4. — Centring Nut of Delivery Roller *a*.

“The sensitising liquid is contained in a trough *h*, which is preferably made of hard rubber. Galvanised zinc, however, if coated with shellac first and, when dried, with an asphalt solution, answers also. The sensitising roller may be either of hard rubber or wood covered with felt or canton flannel. The scraper may be a sheet of glass about 3 or 4 inches wide, and as long as the width of the machine. It is well to have both the long edges cut accurately straight and rounded, and free from nicks. This is, however, a point difficult to attain, hence the author has made use of glass tubing, which may be had perfectly straight and round; this gives the best results. The sheets of glass may be supported in a frame of wood in which it may be easily held perfectly tight, yet which allows the excess of liquid scraped off the paper to freely trickle down into the trough. If the glass tubing is used, it should be cemented into a frame one edge of which has been hollowed out to receive it.

“When very or even moderately thin paper is sensitised, the moistening of the paper allows it to stretch considerably, and the stretching occurs most at the middle of the paper. The result of the stretching is to cause a crinkling of the paper as it passes over the rollers *e* and *t*, and longitudinal creases form which totally spoil the paper. This is obviated by replacing *e* and *t* by rollers which are not cylindrical, but which are thicker in the middle than at the ends; and the thinner the paper, the thicker must the rolls be in the middle as compared with the ends.

“The paper is started on the machine by first winding a couple of hundred yards of heavy manilla paper on the roll *g*, and then carrying the end of this paper through the length of the machine and back again to about the place shown at *k*. Here the paper drawn from the roller *a* meets it, and the two are pasted together. The paper is then run back until it is but a few inches in front of the sensitising roller.

“Power is supplied at *g*, and a speed of about 100 yards per hour is given to the paper. The power must be steady and even, and must absolutely impart no vibration to the machine, otherwise a series of transverse parallel lines will become visible on the paper when dry—due to the fact that the liquid remained in contact for a fraction of a second longer on one spot of the paper than it did on another, and the liquid will have soaked into the paper so much the more the longer the contact. The utmost care must be observed that no solid particles of matter settle in the angle formed by the scraper and the paper, for when this happens, the paper is partially lifted from the scraper, and a long longitudinal streak caused by an excess of sensitising liquid will result.

“The form of machine last described has the advantage that the top may be used as a table. The sides may be screened with oilcloth or other material, thus rendering every part of the machine and paper easily accessible, which is very important, as sometimes the paper does not run perfectly true, because of faulty winding up on its spool, stretching

more on one side than on the other, faulty alignment, etc. Furthermore, the operator has always before him the freshly sensitised paper as it leaves the scraper, and by reason of the arrangement, is enabled to watch over the details, by a close study of which alone is the sensitising of paper, even with a well constructed machine, rendered perfectly successful. It need scarcely be mentioned, of course, that all movable parts of the machine must run easily and freely and without a jar, and all the bearings be kept well oiled and free from dirt."

*Pellet* (blue line on white ground).

This process is perhaps best known by the name of Pellet, who brought it to perfection, though Pellet's formula is a trade secret.

The paper is made as follows (for development, etc., see page 94) :—

A formula for coating due to Pizzighelli is one which the writer can recommend.

Three stock solutions are required :—

A. Pure gum arabic,	. 88 grains.	200 grams.
Water, . . . .	. 1 ounce.	1000 c.cs.
B. Ferric am. citrate,	. 220 grains.	500 grams.
Water, . . . .	. 1 ounce.	1000 c.cs.
C. Ferric chloride (cryst.),	220 grains.	500 grams.
Water, . . . .	. 1 ounce.	1000 c.cs.

The gum solution keeps only a few days, the other two for many weeks, if kept well corked in the dark.

To make the sensitiser take :—

Sol. A. (gum), . . .	20 vols.
Sol. B. (citrate), . . .	8 „
Sol. C. (chloride), . . .	5 „

Add B and C to A, little by little, shaking between each dose. C must be added after B. Reversal of the order is liable to cause coagulation of the gum. The mixture is thick at first, but becomes thinner after a few hours. It keeps in good condition for two or three days.

Fisch\* gives another formula :—

Gum arabic (Senegal),	128 grains.	175 grams.
Water, . . . . .	1 ounce.	600 c.cs.

When completely dissolved, filter through muslin, and take the specific gravity. It should be about 1·090. If more than this, add water little by little, shaking well, and testing with the hydrometer. The solution only keeps a few days.

Tartaric acid, . . .	175 grains.	40 grams.
Water, . . . . .	1 ounce.	100 c.cs.

This ought to have a specific gravity of 1·075 ; if more, add water as above.

Ferric chloride sol. (sp. gr. 1·45).

To compound the sensitiser take :—

Gum solution,	20 ounces.	1000 c.cs.
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Add little by little, shaking well :—

Tartaric acid solution,	1 ounce 6½ drams.	90 c.cs.
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\* *La Photocopie*, p. 15.

Well mix, and add slowly, with constant shaking:—

Ferric chloride	{	2 ounces, 3 drams—2 ounces, 5 drams.
solution,		120–130 c.cs.

Test the mixture with the hydrometer. The gravity should be 1·080: add water (well mixing) until it registers this figure within a division or two.

The paper for the Pellet process must be well sized and calendered to resist the penetration of the sensitiser into the fibre. This is necessary, to avoid blue staining of the ground. Special papers are sold by Steinbach, Blanchet Frères and Kleber, and other makers.

*Coating* is by brushing or floating. For the former, spread the sensitiser as evenly as possible with a large badger brush, working the brush first lengthways and then crossways very lightly, to get a uniform coat. The happy medium between a too thin and too thick coating is what is wanted. The former gives prints of poor vigour, the latter requires a longer exposure to obtain a pure ground.

To coat by floating, Duchochois directs rolling the paper up, sized side outwards, and placing the roll on the solution contained in a dish. The two ends of the roll are slowly drawn out, with the result that the paper gradually unrolls itself and is drawn away coated with the sensitiser. It is dried quickly in the dark, and keeps for a long time preserved from light and damp.

*Ferro-gallic.*—For development with gallic acid (page 99), paper is coated with a mixture containing ferric chloride and tartaric acid with gum or gelatine.



Colas, to whom the perfection of this process is largely due, gives the following formula \* :—

Gelatine, .	14 grains.	33 grams.	10 grams.
Ferric chloride (syrupy),	} 29 „	67 „	20 „
Ferric sulphate, 14 „			
Tartaric acid, 14 „	33 „	10 „	10 „
Water, .	1 ounce.	1000 c.cs.	300 c.cs.

This is applied in the same manner as the sensitising solution in the Pellet process.

Lietze, in his comprehensive treatise on heliographic printing, recommends † the following :—

Gum arabic, . . .	1 ounce.	67 grams
Ferric chloride (solid),	$\frac{3}{4}$ „	50 „
Tartaric acid, . . .	$\frac{1}{2}$ „	33 „
Monsell's salt, . . .	$\frac{1}{2}$ „	33 „
Water, . . . . .	15 ounces.	1000 c.cs.

For Monsell's salt see page 21. Development takes place in gallic acid solution (one part of acid in 320 parts of water).

Another recent formula is Nakahara's ‡ :—

Gum arabic . . .	59 grains.	135 grams.	15 grams.
Tartaric acid, . . .	8 „	18 „	2 „
Sod. chloride (salt),	36 „	81 „	9 „
Ferric chloride, . . .	59 „	135 „	15 „
Ferric sulphate, . . .	39 „	90 „	10 „
Water, . . . . .	1 ounce.	1000 c.cs.	110 c.cs.

\* *Gewerblatt aus Wurtemberg*, 1886, vol. xxxiii. p. 365; Eder's *Handbuch*, 1887, vol. iv. p. 236.

† *Modern Heliographic Processes, Instruction in the Art of Reproducing Drawings, Engravings, etc., by the Action of Light.*

‡ *Photo Chronik*, 1895, p. 125; *The Amateur Photographer*, March 29, 1895.

Dissolve the gum in the water (hot) and add the rest of the chemicals in the order given. Apply the mixture to the paper with a sponge; then, squeezing out the sponge, remove as much as possible.

*Ferro-gallic—Water-bath.*—By incorporating gallic acid or other developing substance with the salts on the paper in such a manner that no reaction takes place between the iron salts and the gallic acid, a sensitive paper is produced which gives a black-line copy merely by washing in water (page 100). There are two methods of manufacture. According to the older, finely-powdered gallic or tannic acid is strewed over the paper which has received the coating of iron salts. According to the more recent method, the coated paper is treated with a solution of gallic acid containing also a substance which prevents the reaction between ferric salts and gallic acid until (when the copy is developed) this restraining substance is largely diluted with water. Hydrochloric, oxalic, and tartaric acids act in this way, and are dissolved along with the gallic acid in a solvent which can be applied to the paper without disturbing the coating of ferric salt.

A formula for the first method is that of Shawcross and Thompson, who took out a patent in 1884 (English patent, No. 8771):—

Gelatine,	.	.	60 grains.	1,500 grams.
Ferric sulphate,	.	24	„	600 „
Salt,	.	37	„	940 „
Tartaric acid,	.	7	„	188 „
Ferric chloride,	.	60	„	1,500 „
Water,	.	1 ounce.		11,000 c.cs.

Finely-powdered gallic acid is dusted over the paper,

which has received a coating of the above solution and has been dried.

Paper to be treated by the second method is given a coating of a somewhat similar solution to the above, and after drying is floated on—

Gallic acid, .	66–88 grains.	150–200 grams.
Tartaric acid, .	22–35 „	50–80 „
Alcohol, .	1 ounce.	1000 c.cs.

Paper prepared by this process develops—so it is stated by Messrs Schering, who are the makers of the paper—very much more quickly than that manufactured by the powder process, owing to the fine state of division of the gallic acid. On immersion in water, the equilibrium existing between this substance and the tartaric or other acid is upset, and the former reacts at once with the ferric salts with which it finds itself in contact.

Paper for ferro-gallic must have a hard surface and be well sized in order to prevent the ground from becoming stained. Hancke (English patent 15,673, 1901) coats cheap porous paper with an insoluble layer of resin, or insoluble gelatine, and on top of this a soluble layer of starch or dextrine, his object being to utilise such cheap paper for the process.

*Brown line*, or *Sepia*, is a silver-iron process analogous to Kallitype. The formula on page 41 answers perfectly for the preparation of papers intended for copies from tracings on the large scale. The following formula has been patented by Arndt and Troost, of Frankfort-on-Main,\* who made paper in 1894 as *Sepia Blitz-Lichtpaus papier*. See also p. 104.

\* English patent No. 20,358, 29th June 1895.

A paper must be used which contains no chlorine ; that made from pure rag is most suitable. The presence of wood pulp is very objectionable.

The sensitising solution contains :—

Ferric am. citrate,	. 35-44 grains.	80-100 grams.
Tartaric acid,	. . 7-9 „	15-20 „
Gelatine,	. . 4-7 „	10-15 „
Silver nitrate,	. . 5-9 „	12-20 „
Distilled water,	. . 1 ounce.	1000 c.cs.

Paper is soaked in this solution and dried ; it keeps unchanged for several months.

A later formula of Dr Laurens is \* :—

- A. Ferric am. citrate (green), 1 oz. 103 gr. 35 grams.  
     Tartaric acid, . . . 62 gr. 4 „  
     Water, . . . 7 oz. 200 c.cs.
- B. Gelatine, . . . 93 gr. 6 grams.  
     Water, . . . 3½ oz. 100 c.cs.
- C. 10 per cent. silver nitrate solution.

A and B are mixed at 103° Fahr. and the silver added with constant stirring. The paper is coated with the lukewarm mixture. The solutions and the paper should be free from chlorides.

Two decompositions probably take place when the paper is exposed to light. Some of the silver nitrate forms (in combination with the gelatine) the dark-colored 'gelatinate of silver,' whilst the second and predominant reaction is that of the reduction of the ferric to ferrous salt, the latter precipitating metallic silver from the silver nitrate.

\* *Photographische Wochenblatt*, 1893, p. 305.

## CHAPTER XI

## MAKING TRACINGS FOR SUN-COPYING

TRACINGS for reproduction by ferro-prussiate and allied processes should be on thin bluish tracing paper. Tracing cloth scarcely gives such good copies and does not take the draughtsman's ink so well as the paper. Whichever is used, a yellowish-colored tracing is to be particularly avoided. Many manufacturers of printing papers supply specially suitable tracing cloths and papers.

Lines, dimensions, etc., should, wherever possible, be drawn in thick Indian ink, and it is always well to add a little chrome yellow or gamboge, or a little of one or other of the various preparations sold for rendering the ink more opaque to actinic rays. The test of a good tracing for sun-copying is to hold it up to a strong light and to closely examine the opacity of the lines.

Lines in colored inks never come out so well as those in Indian ink, unless an exceptional thickness of ink be used, in which case the brilliancy of the color is impaired. Prussian blue should be avoided or, if it is used, must be thickened with an opaque pigment like Chinese white or flake white. Indigo gives better results than Prussian blue, though unfortunately, if applied fairly thick is scarcely distin-

guishable from black. Vermilion is the best color for red.

Wherever possible, it is best to use Indian ink lines in different styles of punctuation in place of colored inks.

It is sometimes desired to color the sectional portions of the printed copies. This offers no difficulty in the case of prints by the Pellet and ferrogallic processes, but for ferro-prussiate prints the sectional portions of the original tracing must be covered with an opaque color like Chinese white. In the printed copy these portions will be practically white, and they can then be colored as desired.

To make a tracing which can be used as a negative for ferro-prussiate paper (giving blue lines) on a white ground, the method of M. Cheysson\* is to be recommended.

Make the tracing in lithographic ink. The ink is prepared by rubbing the solid stick on the bottom of a large saucer. When enough has been thus ground up, a very little distilled water is added (tap water is not suitable) and the whole mixed with the finger. If not of the requisite consistency, add a little more water and grind up with the ink till a dense and liquid mixture results, which is used on the drawing pen exactly like Indian ink.

Let the tracing dry and place on a board covered with one or two thicknesses of blotting-paper. With a soft brush, coat the whole surface of the tracing with a solution of aniline brown (a strong solution of the

\* *Manual des procédés de reproduction d'écritures et de dessins à employer dans le service des ponts et chaussées*, Paris, 1880.

dye made in hot water and allowed to cool). Be careful to get none on the back. As soon as dry, rub the paper over with a tuft of cotton-wool or soft rag moistened with turpentine until the ink lines of the drawing are dissolved away. This leaves the design in transparent lines on a dark brown ground, and the process will yield positive prints (dark lines on white ground) when printed in ferro-prussiate or brown-line processes.

Tracings must on no account be folded or creased: all such marks will show in the copy.

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## CHAPTER XII

### OUTFIT FOR HELIOGRAPHIC PRINTING

THE apparatus necessary for the equipment of a printing house is not very expensive, and comprises printing frames, baths for development and washing, drying arrangements, benches for trimming and mounting copies, and racks for keeping tracings which have or have not been copied. These, and a small room for the storage of sensitive paper, will meet the requirements of the blue printer.

*Printing Frames.*—For daylight work the printing frame consists of a strong shallow frame with a plate-glass front, on which the tracing and sensitive paper

are laid. These are backed up with a thick pad of felt, preferably covered on its under side with vulcanised rubber sheet. The back of the frame is made in several sections, pressure on each being applied by means of a series of vertical, spiral, or other springs, held in place by upright pegs fixed to the back itself. These springs exert downward pressure on the back of the frame and upward on the cross-bars, which are hinged to one side of the frame and secured by a catch to the opposite side. A properly constructed frame is a *sine qua non*, since it is most essential that the tracing and sensitive paper shall be pressed into firm and uniform contact. Any defect in this respect means blurred lines in the copy.

A cheaper form of printing frame which does not involve the use of a glass front is described by C. B. Talbot\* as specially suitable for field or other purposes where portability is a consideration. Two end boards (fig. 5) having an arch-shaped groove, secured to a hinged frame at the back, have placed therein the ends of some loosely-fitting tongued and grooved boards, the surfaces of which are formed to the radius of the curve (3 or 4 feet). Each board is about 3 inches wide and supported loosely on a bridge at the middle of the back of the same shape as the grooves. About one third of the width of the frame is hinged. The edge of the tracing is slipped through any crack in the tongue and grooves corresponding to its width. On the narrow side, the boards near the edge are made of different widths, say,  $2\frac{1}{2}$ , 3,  $3\frac{1}{2}$ , 4 inches, so that one edge of the tracing being placed in a given

\* *Anthony's International Annual*, 1889-90, p. 235.



crack, the other edge is pretty certain to find a suitable hold on the other side of the hinge. The tracing, with, of course, the paper beneath it, is stretched by pushing the board closely, allowing the tracing to slip easily though firmly through the cracks between the boards until the desired tension is given; then bringing the hinge down and locking it at the back to the frame.

The pneumatic printing frame of H. Sack, Düsseldorf-Rath, in which pressure is applied to the back of the sensitive paper by an inflated air-cushion, is used

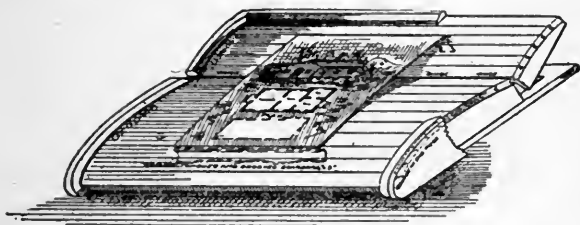


FIG. 5.—Unglazed Printing Frame.

more on the Continent than in England. Messrs Bemrose are the British agents.

*Printing by Electric Light.*—The arc light is now used extensively for printing, and under many circumstances is superseding daylight altogether. This is not surprising, since in the winter months daylight is available, for practical purposes, only two or three hours in the middle of the day, and several days may be spent before a ferro-prussiate print can be obtained—if the paper is not spoilt by undue exposure to the damp weather in the meantime. For reasons of economy of time, labor

and material, therefore, artificial light is far superior to daylight, especially in towns where the light is robbed of a large part of its actinic power by the overhanging haze. The artificial light installation

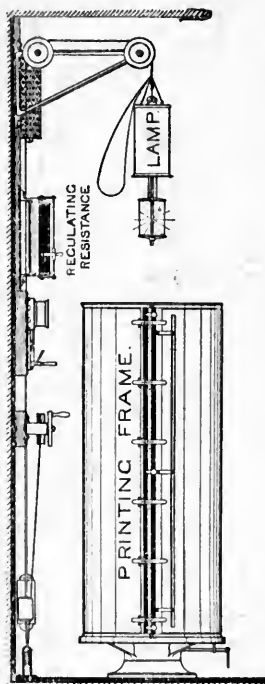
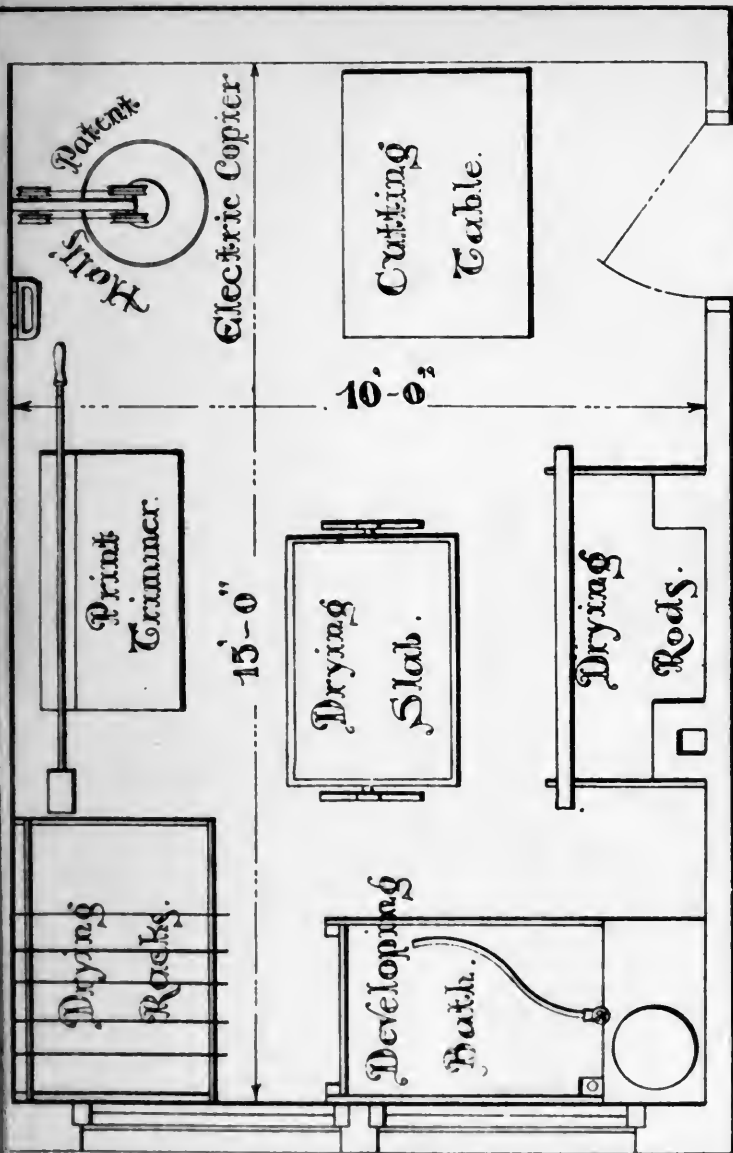


FIG. 6.—Hall's Lamp.

likewise economises space and makes it easy to take off copies even in a drawing office without appreciable inconvenience.

The outfit consists of a cylinder (made in halves) of polished rolled plate glass. The tracing with the sensitising paper behind it, is wrapped around the outside of the cylinder by a canvas apron. The arc lamp suspended above the centre of the cylinder is lowered, automatically or by hand, into the cylinder and kept moving up and down, within a determinable range for as long as is necessary for exposure.

Tracing and paper are inserted very rapidly into place. They are rolled up together, with the tracing on the inner side of the roll. The latter is then placed between the apron and the glass and, by withdrawing the hand, unrolled in contact with the glass. The loose end of apron is then strapped to



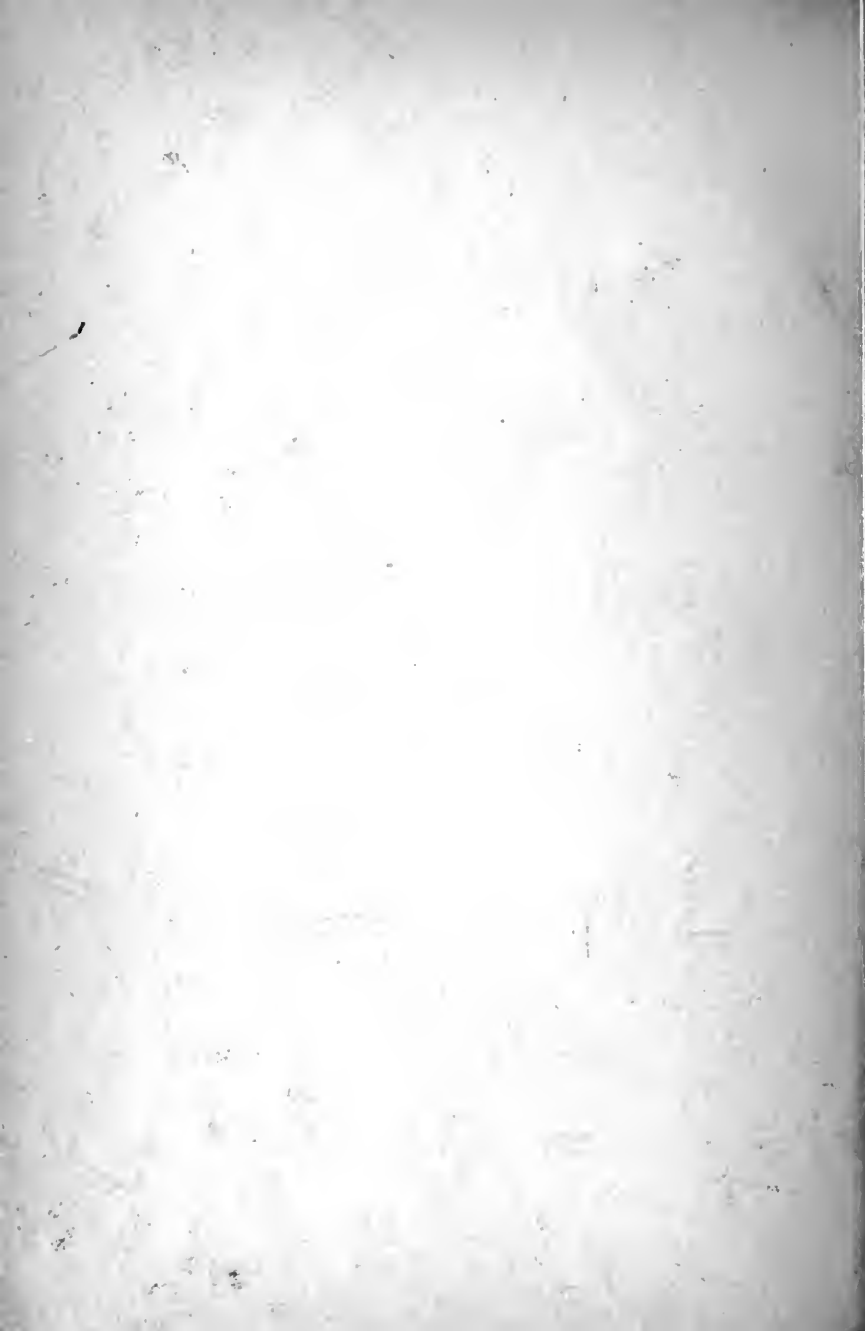
Arrangement of Photo-Printing Room

WITH

HALL'S PATENT ELECTRIC COPIER.

PERMANENT BLACK LINE PHOTO-PRINT TAKEN BY ELECTRIC LIGHT.

B. J. Hall & Co., 39, Victoria Street, London S.W.



the cylinder and contact made by a lever-tightening gear, which squeezes tracing and paper very tightly and smoothly against the glass.

The lamp descends slowly or quickly, according as the paper is rapid or slow, this range of speed being necessary to equally illuminate the tracing. In B. J. Hall's lamp (fig. 6) the gear regulating this movement is very simple, and in the lamps as now made is outside the supporting pillar.

In addition to the automatic movement, which is actuated by the lamp itself, there is a hand adjustment.

The following times are given by Hall for fully exposed copies from two double-elephant tracings on clear blue-slate tracing paper, using the No. 1 lamp :—

Very slow ferro-prussiate paper (blue print)	8 minutes.
Ordinary ferro-prussiate paper	3 „
Rapid ferro-prussiate paper	1½ „
Ferro-prussiate linen	4 „
Black line water-bath paper	7 to 8 „
Sepia negative from tracing	3 „
Sepia negative from inked drawing	15 „
Sepia negative on Whatman's paper	15 „
Sepia positive from negative	8 „
Sepia positive linen, from negative	12 „
Pellet (blue line white ground)	1½ „

The Hall lamp is supplied in four standard sizes :—  
No. 1 is a 10-ampère lamp, taking 120 volts across the arc, used for continuous current ; No. 2 is a 12-ampère lamp, taking 75 to 90 volts across the arc,

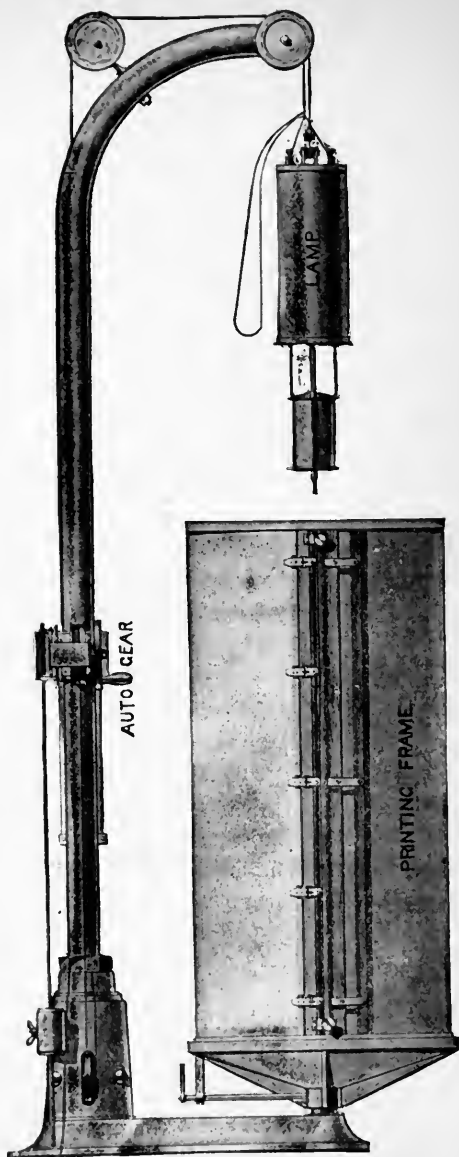


FIG. 7.—Hall's Lamp.

used for continuous current ; No. 3 is a 20-ampère lamp taking 75 to 90 volts across the arc, used for continuous current ; No. 4 is a 15-ampère lamp, taking 75 to 90 volts across the arc, used for alternating currents.

Taking the time for exposure as unity when lamp No. 1 is used, No. 2 equals 1.75, No. 3 equals 1.25, No. 4 equals 2. The alternating lamp is thus the least satisfactory, and the most expensive in energy for photographic purposes.

Halden's lamp can be turned into the horizontal position for the more convenient filling and emptying of the frame ; the tracing lies on the glass plate (when the frame is horizontal) while a fresh piece of sensitive paper is inserted.

A machine (Spaulding's patent) is said to be used in America under the name of the 'Federal,' as shown in fig. 8. The tracing and sensitive paper are fed round a large wooden drum around which a transparent apron is tightly drawn. The drum is moved by connection from shafting or by an electric motor. The apron is wound from a lower roller to an upper one, and back by hand. Three arc lights concentrated by a reflector are said to expose the paper as it passes over the illuminated field.

An electric lamp, intended for projection but suitable for printing in small sizes, is made by Grass & Worff, Berlin. It is made for continuous or alternating current, 110 or 220 volts (fig. 9).

Very long tracings are not easily printed in the ordinary frames. The suggestion has been made

by Cleaves\* to print them around a circular drum having a slit in its side to allow of access to two rollers in the interior. The tracing and sensitive paper are wound together round one roller, brought out through the slit, taken round the drum, and

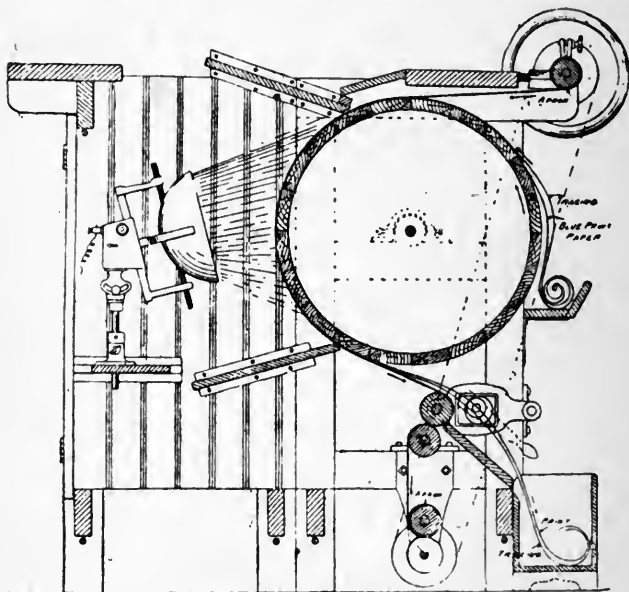


FIG. 8.—Spaulding's Rotary Printer.

stretched tight by means of the second roller. The drum is rotated during printing, and after exposure a second length of tracing and paper is unwound from the first roller whilst the exposed portion is coiled round the second.

\* Memoir by Prof. R. H. Thurston, Washington Meeting of Mechanical Engineers, 1887.



*Washing and Developing Baths.*—For washing in plain water, the most satisfactory material, taking price into consideration, is zinc, and baths of this material can be used for developing ferro-prussiate

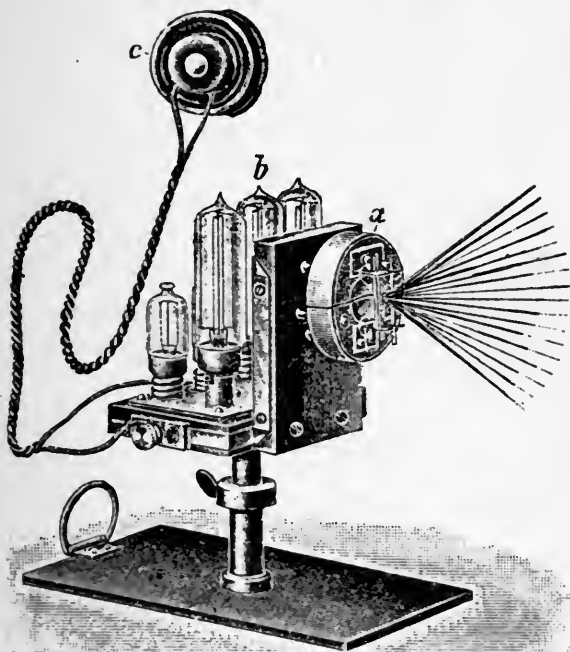


FIG. 9.—Grass & Worril's Lamp.

and ferro-gallic and brown-line prints, and for the final washing of copies on Pellet paper. They must not be used for the ferrocyanide and acid bath required in the Pellet process, for which lead-

lined wood trays or papier-mâché are necessary. Wooden wax-coated trays are readily made at a small cost, and can be used for practically all the blue printers' solutions. Yellow pine is the best material, being dovetailed together, made quite hot before a fire, and melted paraffin wax poured in as evenly as possible: any irregularities can be corrected with a hot iron. The outsides of the trays should be varnished with shellac varnish. Another suitable protective coating for the inside is:—

Brown resin, . . . . .	4 parts.
Bees-wax, . . . . .	1 part.

These are melted together and applied hot.

The baths should be of ample size: it is a mistake to stint matters in this respect. A safe rule is to have them six inches larger than the largest tracing which the printing frames will accommodate. They are arranged on trestles with a water tap (with rubber tube attached) at one end. In winter an oil or gas stove or coil of steam pipes is required under the Pellet developing bath and others. Each bath should be kept for one particular purpose and no other. Neglect of this is the cause of much trouble in the matter of stains.

For office use, where space is limited, B. H. Thwaite\* prefers to use a vertical washing bath for ferro-prussiate prints, suspending the copy in the water from a light lath laid across the top of the bath (fig. 10).

*Drying Arrangements.*—An efficient drying ap-

\* *Proc. Inst. Civ. Eng.*, 1885-86, Pt. IV. p. 812.

paratus is described and illustrated on p. 61, and a small room—or a corner of a developing house partitioned off—fitted up with a similar arrangement and furnished with a coil of steam pipes in the base and an outlet for air above, will speedily dry prints, whatever may be the state of the weather. Otherwise a series of drying rods or lines with a gas stove fixed close at hand is a practical though less

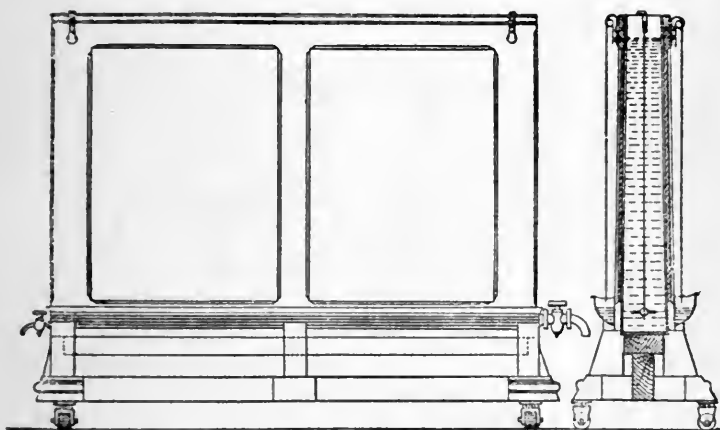


FIG. 10.—Vertical Washing Bath. (B. H. Thwaite.)

certain method. For attaching prints to the drying rods, clips, in shape of an inverted  $\cap$ , are used, or photographers' 'push-pins' are very convenient. For attaching to lines, the usual clips are employed (fig. 11).

*Other Fixtures.*—A couple of solid tables for trimming and mounting prints are necessary items in the outfit, as are also some racks in which to file

tracings which await printing or are being retained for future use.

A small room kept warm and dry should be set apart for the storage of the sensitive papers, the opened rolls of which should be stored, when not in use, in light-tight tin cases.

*The illumination* of the place used for developing must be subdued. Weak daylight is very generally used with satisfactory results. If sunlight has to

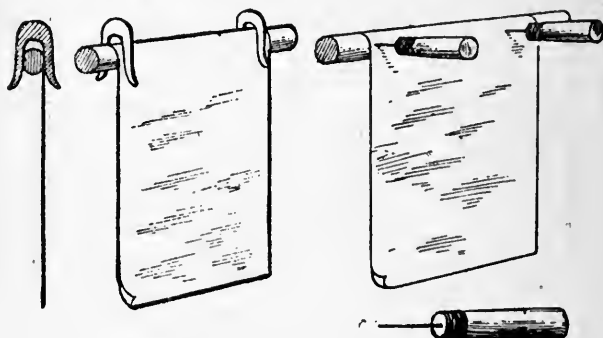


FIG. 11.—Drying Clips and Pins.

be excluded from any window, yellow tissue paper pasted on the glass will be found to answer.

*The arrangement of the printing house* will, of course, depend very largely on local conditions and requirements. Where space and an open view are available, a yard in front of the premises, into which the printing frames can be wheeled, is convenient. In towns it is often necessary to utilise the roof of a building for printing purposes. In offices to which daylight has no very free access, the exposure is

shortened by the use of two reflectors, one outside the window, face upwards at an angle of  $45^\circ$  to the horizontal, and one inside, above the window and face down, at the same inclination. The light from the sky is reflected from the first mirror to the second and thence to the printing frame. Sometimes the latter can be raised to the roof and exposed to the direct light of the sky, reaching it through a fanlight.

*Water Supply.*—The quality of the water used for washing blue prints is a point which may in certain cases require attention. It is pointed out on page 145 that weak alkalies—even calcium carbonate in solution—decompose *Prussian blue*, whence it follows that the ‘softer’ a water is the more suitable for the purposes of the blue printer. For practical purposes the quantities of carbonate of lime and other salts in most town waters have no appreciable action within the limits of ordinary manipulation. Cases do, however, arise where the water makes itself known by its weakening action on the blue ground or line of the print. An instance was recently brought to the writer’s notice where a printing house was being supplied with water containing over 40 grains of carbonate of soda (expressed as  $\text{Na}_2\text{CO}_3$ ) per gallon, which speedily reduced the intensity of the prints. The application of a chemical test (the estimation of the alkalinity, etc.) will at once tell whether a water supply is unsuitable in this respect.

## CHAPTER XIII

## FERRO-PRUSSATE, OR WHITE LINE ON BLUE GROUND

*White Line on Blue Ground.*—The making of the sensitive paper has been described on pages 11 and 59. The tracing is laid face down on the glass of the printing frame, and a piece of sensitive paper, of such size as to project about two inches all round, laid upon it. The felt pad and the back of the frame having been fixed, the whole is exposed to light, and the progress of printing judged by observing the outside portion, which gradually changes from yellowish-green through bluish-green and slaty-grey to olive-green, the tint corresponding to correct exposure differing slightly with different brands of paper. A minute or two's exposure beyond this point will (in the case of ordinary tracing paper or cloth) leave the print properly exposed. Prints from thicker and more opaque paper must, of course, receive much longer exposure, and it is generally necessary to examine the print itself.

Exposure may be gauged by meter, and for this purpose a very convenient instrument is Wynne's print meter. The meter (fig. 12) consists of a small metal case with a front of opal and a hinged back, carrying inside a sensitive paper. Behind the opal face is a plate, perforated with a series of diaphragms

which serve to admit different intensities of light to a series of figures on a glass plate, which, when the meter is closed, is pressed into contact with the sensitive paper on the back of the instrument. On exposing the meter to light, the light gradually impresses the graduated scale—which is numbered 1 to 16 and then onwards A to P—on the sensitive paper.

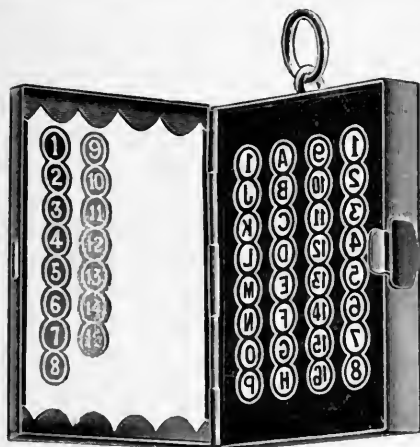


FIG. 12.—Wynne's Print Meter.

In using the meter for timing blue prints, a preliminary test exposure is made, paper and meter being exposed simultaneously to the same light. As soon as the print is correctly exposed, the last number (just readable) registered on the meter is noted, and, in all future work with the same brand of paper and quality of tracing cloth, the print can be taken in as soon as the meter registers that particular number. Other brands of paper will require a different meter number,

but, these once ascertained (by a test exposure), exposures can be made with certainty. Several frames can be timed with one meter if exposed at the same time and to the same light. The meter can be used also for Pellet, ferro-gallic, and other processes.

*Development.*—On removal from the frame the print is washed in water. Slowly running water is best, but in its absence a soft brush or sponge is very efficient in removing the surplus salts. A thorough treatment in this way in the first water, followed by two or three short soaks in clean water, will be sufficient. Too little washing causes veiling of the lines afterwards: too much, a general weakening of the copy. Fifteen to twenty minutes is generally quite sufficient. In winter, a little more.

In cases where a print is required at the earliest possible moment, lay the copy in the bottom of the washing bath and apply a vigorous stream of water from an india-rubber tube (squeezing the end between the fingers or using a jet) to both back and front of the paper. A minute or two's treatment of this kind suffices to get rid of practically all the soluble salts.

After washing, the copy is rolled up wet and the roll stood up to drain: then opened out and hung up to dry in a subdued light.

*Over-printed copies* are given a somewhat longer washing, which, if exposure has not been greatly excessive, has the effect of clearing the lines; otherwise, it is best to throw away the prints rather than to treat them with potash or other chemical reducing agents, the results of which are generally disappointing.



*Under-printed copies* can be somewhat improved by immersion in a weak solution of an iron (ferrie) salt, though no great intensification must be expected. Scherings make up a solution, specially for use with their blue paper, under the name of *Verstärkungslösung für Blausäures Eisenpapier*. Apparently it is an iron salt. The well washed print is placed in—

Stock sol.,	.	2·5–5 mins.	5–10 c.cs.
Water,	.	1 ounce.	1000 „

for about five to twenty seconds, and, as soon as the blue of the ground has deepened sufficiently, is washed in clean water and dried. The weak bath keeps several days. The usual experience is, however, that intensification is of little use, and that an under-exposed print had better be thrown away and a second copy made.

Additional lines are put in with the oxalate of potash solution (given on p. 115) thickened with a little gum arabic.

Existing lines are removed by Prussian blue applied with a fine camel's-hair pencil.

## CHAPTER XIV

## PELLET, OR BLUE LINE ON WHITE GROUND

THE Pellet paper, the manufacture of which is described on p. 68, is much more sensitive than most brands of ferro-prussiate, and must only be handled in quite a subdued light. The exposure in summer sunlight is about seventy seconds, but, as the image is only faintly visible, it is necessary to judge of its completion by a trial method or by meter, as described on p. 90.

*Trial Method.*—When the paper is being placed in the frame, a test strip of tracing cloth is placed alongside the tracing. This strip (which may measure about  $6 \times 2$  inches) has ruled upon it half a dozen or more lines in Indian ink or vermilion, corresponding as nearly as may be with the lines of the tracing, the cloth also being of a similar quality. A stock of these strips, in different thicknesses of ink and on different cloths, should be kept at hand, and with a little experience it is easy to select a suitable one. The strip is laid near the edge of the frame, and a few strips of sensitive paper laid crosswise behind it with the free ends projecting from the frame. When the exposure is judged to be about complete, a strip of paper is pulled out and the frame swung over. The strip is dipped in the ferrocyanide bath for

about thirty seconds. The lines should develop to a vigorous blue, and the ground show no sign of blue stain. If the ground is blue, continue the exposure and test again. If, on the other hand, the lines are feeble and broken, exposure has been too long.

*Faking during Printing.*—During exposure to light a good deal can be done to make the most of inferior tracings by masking portions of the latter. Very often one part of the tracing is made in thinner ink than another, as may be seen by holding the tracing up to strong daylight, and the thinner parts will be saved from being feebly reproduced by masking with a soft dark cloth which can be readily fitted to the area desired. Then the outside parts of the tracing are liable to get dirty and to give a bluish ground, if exposure be timed for the lines; but if the central lined portions be covered, an additional exposure can be given to the outside, which will ensure a pure white ground in the copy.

*Development.*—The print is developed on a strong solution of potassium ferrocyanide (yellow prussiate of potash).

Yellow prussiate,	1 ounce.	1 pound.	100 grams.
Water,	10 ounces.	1 gallon.	1000 c.cs.

Use warm water for dissolving the salt and see that the temperature of the bath does not fall below about 60° Fahr. Some makers advise rather stronger, and others weaker solutions than the above. Their printed instructions will supply the specific strength. The developing tray should contain this solution to a depth of from  $\frac{3}{4}$  of an inch to 1 inch.

Before development, turn up the edges of the print all the way round about half an inch, so that it forms a shallow tray. In this shape it is removed and floated on the developer, the raised edge preventing the access of developer to the back. As soon as laid on the liquid, the whole back is smoothed down with the palm of the hand so as to bring every portion into contact with the liquid (fig. 13). Then it is raised by the two nearest

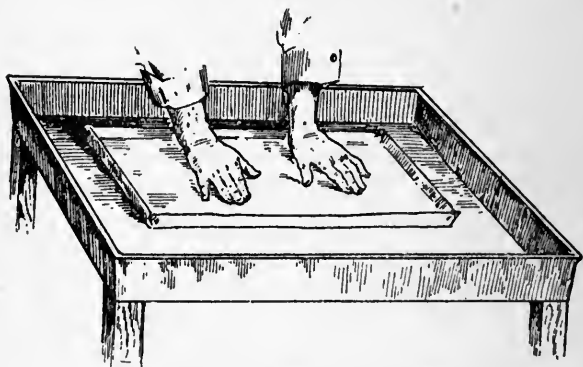
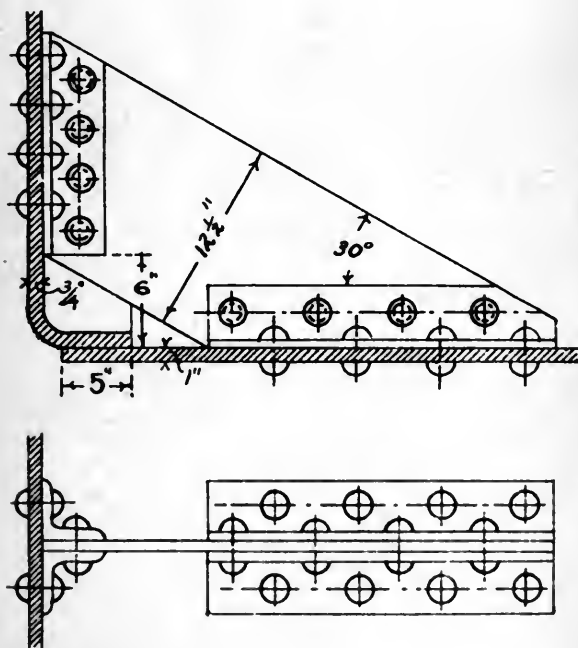


FIG. 13.—Developing Pellet Papers.

corners, and held up for examination. All the lines ought to be visible in vigorous blue. The time from the moment of flotation to the removal from the developer should not exceed about thirty seconds. Too long on the developer produces spreading of the lines.

*Washing.*—Next pass the print into a bath of water, and flush it quickly back and front from the india-rubber tube. This is merely to stop the action

Photo - print from a tracing  
by  
Norton & Gregory's  
New Black Line Process.





and remove most of the ferrocyanide, and only occupies a few seconds.

*Acid Bath.*—The print next passes into an acid bath (sometimes referred to as the ‘fixing’ and sometimes as the ‘bleaching’ bath). This is made (in an earthenware vessel) as follows :—

Sulphuric acid (sp. } gr. 1·98), . . . }	1½ ounce.	40 c.cs.
Water, . . . . .	40 ounces.	1000 „

Add the acid to the water, and not *vice versa*. Much heat is produced on mixing, so that a glass vessel must not be used. Instead of sulphuric acid, hydrochloric acid can be used :—

Hydrochloric acid, . . .	4 ounces.	100 c.cs.
Water, . . . . .	40 „	1000 „

These are average strengths, but the makers’ directions will give those which they consider best for their papers. Keep the prints in this bath, face up, for not more than five or six minutes, occasionally stirring the liquid with a wooden spoon or with a rag tied to a stick. This bath soon turns a deep blue, but retains its solvent properties (for the insolubilised gum) for a long time.

*Final Washing.*—On its removal from the acid bath the print is covered with a deposit of light blue color, derived from the oxidation of the white precipitate produced by ferrocyanide on ferrous salts. This deposit is only loosely adherent, and is washed away by subjecting the print to a stiff jet of water.

A soft brush can be used in default of a strong

enough water pressure, but requires gentle handling to avoid weakening the lines. Be particular to keep this washing bath clean by regularly scrubbing it with potass solution and a hard brush. Wash the print in running water or several changes for a quarter of an hour, and dry.

*Defects, their Causes and Remedies.*

*Blue Stains in Patches.*—1. Incomplete contact of the print with the developing solution.

2. Developer getting on the back of print.

3. From stained fingers, while being finally washed.

*Remedies.*—Remove the blue stains with the oxalate solution given on p. 115.

Be careful to clean the fingers in weak potass solution after dabbling in the acid bath.

*Uniform Blue Ground.*—Under-exposure.

*Faint and Broken Lines.*—Over-exposure.

*Spread and Blurred Lines.*—Under-exposure. Too long development. Too strong developer.



## CHAPTER XV

## FERRO-GALLIC, OR BLACK LINE ON WHITE GROUND

THE manufacture of the sensitive papers has already been described on page 72.

GALLIC-BATH PROCESS—*Exposure*.—The paper is very much slower (about five times) than Pellet paper, and requires, in summer sunlight, an exposure of about five minutes. The exposure is judged by (1) noticing when the portions of paper projecting outside the tracing become white. A corner of the sensitive paper is folded over, so that the white back of the paper provides a standard for comparison. (2) Test strip as described on p. 94, the strip being immersed in the gallic-acid bath. (3) Meter (p. 90). The writer prefers (2) and (3) to (1), which, with tracings of yellowish color, is liable to give under-exposed proofs. Whichever method is used, the correctly exposed copy is seen as yellow lines on a white ground. The sooner it is developed the better, but it should certainly not be kept over-night.

*Development*.—Gallic acid is the developer generally used, in conjunction with some substance to help keep the ground clear. Alum or oxalic acid (the latter in small proportion) is used for this.

An average formula is :—

Gallic acid,	.	.	2 ounces.	12 grams.
Alum,	.	.	2 „	12 „
Water,	.	.	1 gallon.	1000 c.cs.

Mix in warm water twenty-four hours before use. Immerse the print in the liquid for about three minutes. The copy develops at once to intense black lines on the ground, which is never quite white, but always has a pale violet tint. Wash in running water for a few minutes, drain, and dry.

*Defects and Causes.*—Violet ground with thick and blurred lines—under-exposure. Faint and broken lines—over-exposure.

**WATER-BATH PROCESS.**—Exposure takes place just as for the gallic-bath paper, and development must follow on the same day.

*Development.*—Wash in running water for ten minutes or so. Under- and over-exposure cause the same defects as with gallic-bath paper.

Violet spots, lines, and unnecessary dimensions are removed by a weak solution of oxalic acid.

The directions given for the use of the ferro-gallic paper made by Messrs Messerli of Zurich contain a number of useful hints from which the following are quoted.

The pressure pad, whether of felt or cloth, is liable to become damp, and, when placed directly on the back of the paper, not only spoils the ground of the paper, but renders a much longer exposure necessary. This explains the considerable difference in sensitiveness sometimes noticed between pieces of paper from

one and the same roll. The moist condition of the frame is responsible for these irregularities, and not, as the printer may be inclined to think, a want of uniformity in the paper.

The fact, too, is frequently overlooked that the much weaker action of winter sunlight on the paper is in part due to the absence of heat rays, and that, if the pressure pad of the frame is thoroughly warmed, exposure takes place appreciably more quickly. Before ten in the morning and after one o'clock, winter sunlight is very weak.

It is a mistake to be over-economical with the developer, which should be renewed as soon as the printer notices that the developing bath is becoming exhausted. An overworked bath will not give an intense black tone.

A cause of failure with the ferro-gallic process is in floating the copy on the developer or in developing by drawing through the solution. Total immersion is necessary. In the after-washing, the copy must on no account be allowed to remain long in water containing developer. The best way to wash is to hold the copy for five minutes under a rose jet, so that the water continually passes off.

Insufficiently exposed prints can be corrected by applying a 2 per cent. solution of tartaric acid with a sponge, and as soon as the dark ground has given way, by well washing with water. This treatment will frequently be found of service, and the solution should find a place in every printing house.

When testing a fresh batch of paper, the fact should be borne in mind that the first yard or so

of the roll seldom gives such good prints as the remainder, and the inferiority of the first portion is the more noticeable the longer the paper has been kept. A freshly made developing bath should be used, and if the paper from the first or second yard's length does not give good results, about half the paper should be unrolled and a piece exposed from the middle portion. If this likewise gives poor results, the paper may be assumed to be at fault.

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## CHAPTER XVI

### BROWN LINE ON WHITE GROUND

THIS paper, made as described on page 73, gives from an ordinary tracing a copy in white lines on a deep brown ground, prints very rapidly, and requires very simple treatment after exposure. The brown color of the deposit makes the process a very suitable one for preparing several paper negatives from a single tracing, each of which can be put in hand to give copies in blue line on a white ground (on ferro-prussiate paper), or brown lines on a white ground if the 'brown' paper itself be used. For getting a number of prints from a tracing which is wanted at once for some other purpose, the process is therefore most useful.

Moreover, part of one tracing can be combined in

the copy with part of another by preparing separate sepia negatives, pasting the parts required together, and taking copies. In this way the sepia negative is useful for taking off copies from a tracing part of which has to be modified from time to time.

A very much better result can very often be obtained *via* a sepia negative and a 'negative' paper than by a 'positive' paper printed direct from the tracing.

*White Line on Brown Ground.*—The tracing and paper are placed in the frame just as for a ferro-prussiate print and exposed to light. The time of exposure in summer sunlight is from thirty seconds to six minutes. The appearance of the print when fully exposed is a clear brown: it gains vigour somewhat in washing and fixing.

*Washing.*—Wash the print for about five minutes in running water.

*Fixing.*—The fixing bath contains:—

Hypo, . . .	7 grains.	4 ounces.	20 grams.
Water, . . .	1 ounce.	1 gallon.	1000 c.cs.

and in this the print is immersed for about a minute. The fixing solution can be applied, if more convenient, with a sponge or brush.

A fixing solution of—

Soda sulphite cyst., . . .	1½ ounce.	150 grams.
Water, . . . . .	10 ounces.	1000 c.cs.

gives a print of darker color and more opaque to actinic light than the hypo (Namias). But it is at least twenty times the cost of hypo.

*Final Washing.*—Well wash for about fifteen minutes, and dry.

*Brown Line on White Ground.*—The ‘brown ground’ copies obtained as just described can be used for printing positive copies. A thin paper is best for this purpose, for the sake of rapidity of printing, but a thicker paper can be rendered translucent by means of castor oil, as described on page 115. The brown-ground copy is treated exactly like a tracing, and exposure and fixation of the copy proceeded with as above described.

To remove brown lines from the ‘white ground’ prints, or to insert white lines in the ‘brown ground’ prints, use a solution as follows:—

Sat. sol. of potass	}	15 mins.	35 c.cs.
cyanide in water,			
Sat. sol. of iodine	}	5 „	12 „
in alcohol,			
Water,		1 ounce.	1000 „

*Note.*—Since the paragraph on page 73 was written, it has come to the writer’s knowledge that the first patent for a sepia process was taken out by Henry Shawcross in Paris, March 18th, 1889. Shawcross took out a similar patent (18,531, 1892) in England, but did not mature it.

## CHAPTER XVII

## MINOR HELIOGRAPHIC PROCESSES

A NUMBER of processes of minor importance are described in this chapter. Considerations of cost or of skill demanded for working them have prevented most of them from coming into general use.

*Willis's aniline process* gives dark lines on a white ground from an ordinary tracing, and depends on the fact that aniline reacts with chromic acid to form a blue-black coloring matter. It has been used in engineering works to a slight extent.

Paper is coated with a chromate mixture and, after exposure, is developed in aniline vapour. Sensitise a hard paper (Steinbach) by floating for one minute on—

Potass bichromate, . . . . .	1 part.
Phosphoric acid (sp. gr. 1.24). . . . .	10 parts.
Water, . . . . .	10 „

Dry quickly, and expose on same or next day. In summer sunlight the exposure required under a tracing is about three minutes. The copy appears in yellow lines on a greenish ground.

To develop, the print is placed on the bottom of a shallow box, to the lid of which are pinned several

sheets of blotting-paper, soaked in a mixture of aniline oil and benzene :—

Aniline, about	.	.	.	.	1 part.
Benzene,	.	.	.	.	15 parts.

More aniline accelerates development. The solution is spread evenly on the blotting-paper and the print left in the box to gradually develop. The correctly exposed copy commences to appear after a few minutes and gradually gains strength. The final tint of the copy is influenced by the time of development. Long exposure to the aniline gives brownish-black, whilst the shorter the development the bluer the color. The prints are washed in water for a few minutes. During this treatment they occasionally turn green : add a few drops of ammonia to the wash water. In the industrial use of the process development is accelerated by employing a steam bath to volatilise the aniline.

*Poitevin's process* utilises the fact that gelatine mixed with a ferric salt is insoluble in water, but becomes soluble when the mixture is exposed to light.

The following working details are due to Abney :— Prepare a 6 per cent. solution of gelatine and add sufficient of a suitable pigment. Float paper on the warm mixture and sensitise by immersion in—

Ferric chloride,	.	44 grains.	100 grams.
Tartaric acid, .	.	13    "	30    "
Water, .	.	1 ounce.	1000 c.cs.

Dry in the dark, expose with the aid of an actinometer, and develop in hot water. The process



gives a copy in dark lines on a white ground from a tracing, and while it furnishes most excellent reproductions, requires great care in manipulation.

Ferric-colloid processes have been very little investigated, although they offer a promising field for heliographic papers.

According to Lux,\* ferric chloride and tartaric acid is the best iron mixture, and one part of anhydrous ferric chloride should be used to every four parts of gum arabic or five parts of gelatine. One formula is as follows:—100 parts of gum arabic are dissolved in 200 parts *cold* water, 10 parts of tartaric acid added, and then in small doses ferric chloride solution equivalent to 25 parts  $\text{Fe}_2\text{Cl}_6$ . This solution is ready for use twenty-four hours after mixing, but reaches its maximum sensitiveness in about three weeks. Lux adds pigment to it to make the coating mixture, taking one part of solid pigment to about three to four parts of solution.

*Chromate Pigment Processes.*—The insolubility, etc., conferred upon gum or gelatine, when exposed to light with potassium bichromate (see p. 142) is the basis of several processes of this kind. They give copies in white lines on a dark ground. The first two of the processes for which we have space depend on the insolubilisation of gum.

Prepare—

Gum arabic, . . .	35 grains.	80 grams.
Lampblack, . . .	9 „	20 „
Water, . . .	1 ounce.	1000 c.cs.

\* Dr Lux, *Deutsche Photographen Zeitung*, 1903, Nos. 35 and 37, pp. 533 and 563.

Spread this mixture with a broad brush on the paper, dry, and sensitise immediately before use with—

Potass bichromate, . 55 grains. 125 grams.

Water, . . . 1 ounce. 1000 c.cs.

This solution is liberally applied to the back of the paper, which is allowed to stand for a few minutes, and the coating then equalised with a brush just moistened with sensitising solution. Coating can be done in daylight, but the paper must be dried in the dark. The pigmented side of the paper is laid in contact with the tracing, and exposed to light till the lines of the drawing are visible on the back. This requires from ten to twenty minutes in summer sunlight. The exposed copy is dipped for a minute in pure water and laid, pigment side up, on a glass plate. The surface is rinsed with a jet of water, removed from the water, and the soluble parts of the image gently dislodged with a soft brush. This leaves the copy in yellow lines on a black ground. It is next soaked in water for several hours to dissolve the chromium salts, washed in clean water, and dried. To obtain positive copies (dark lines on white ground) a negative tracing must be prepared (p. 102).

Gelatine is used in place of gum in a similar way.

Positive copies are obtained from tracings by a variation of the method due to L. von Itterheim :—

Gum arabic, . . 110 grains. 250 grams.

Potass bichromate, . 31 „ 70 „

Alcohol, . . . 5 mins. 10 c.cs.

Water, . . . 1 ounce. 1000 „

Smooth sized paper is coated with this mixture, which keeps a few days. It is exposed under a tracing for five or ten minutes, and washed in water till the lines of the drawing look engraved. It is then dried, and given an even and thin coat of shellac and lampblack.

Shellac,	.	.	.	.	.	1 part.
Lampblack,	.	.	.	.	.	3 parts.
Alcohol,	.	.	.	.	.	20 „

Apply this with a sponge and, when dry, immerse the paper in—

Sulphuric acid,	.	.	.	.	.	2-3 parts.
Water,	.	.	.	.	.	100 „

until the superfluous black can be removed by gentle rubbing.

In this process a ground of insoluble gum is formed with the lines of the tracing in soluble gum. These latter are removed by the washing, and when the shellac is applied, the bare paper retains it whilst the ground is cleared of pigment by the weak acid. The method is said to be commercially worked in Vienna (Eder).

According to Valenta\* the paper for Itterheim's and like processes must be smooth and well sized in order that the lights shall not retain the soluble gum and chromate, and also that the insolubilised gum-chromate may be readily removed in the acid bath. To test the paper, some lines are ruled on it with the mixture of shellac and lampblack to be

\* *Photographische Korrespondenz*, Jan. 1904.

used in the process itself, these being applied with a pen or a fine brush. When they are dry the paper is placed in dilute hydrochloric acid (1 in 50), and left there for some hours. If the strokes are easily removed on rinsing in a stream of water, or gently treating with a soft wet brush, the paper is unsuitable. As a test for the proper sizing of the paper a double cross is drawn on the paper with a



pen and a brilliant ink such as Chemnitz violet copying ink, and left to dry. No signs of the cross should be visible on the back of the paper, and the edges of the lines should be quite sharp. If a smooth paper withstands both tests it is usually well suited to the process.

These methods give copies of fine pigment black on a white ground *from negatives* of the tracings. As worked by B. J. Hall & Co., who issue a commercial paper based on this principle, the *modus operandi* is greatly simplified. The paper is printed from the negative copy, yielding a faint brown image on a yellow ground. Lampblack in a slightly moist state is then rubbed all over the print with a pad, and the paper then developed in hot water. The ground of soluble gelatine comes away, but the lines remain as fine pigment black. Messrs Hall claim that the sensitive (*i.e.* bichro-

mated) paper will keep for six months before use as ordinarily wrapped.

Pigment paper of this description is supplied by Halden & Co., Manchester, Bemrose & Co., Derby, and possibly by others. Norton & Gregory, Westminster, prepare copies by a secret process of this kind which they claim to be a development of the chromate pigment process, differing from it in the colloid used, if not in other respects. They do not supply the sensitive paper.

*Anthrakotype* depends on the loss of tackiness of gelatine on exposure to light with bichromate. It was devised by Sobacchi in 1879 : we are indebted to Pizzighelli for precise working details. The process gives a positive from an ordinary tracing, and lines of any desired color can be obtained by selecting a suitable pigment.

Hard gelatine is mixed with cold water in the proportion of one part of gelatine to thirty parts of water, allowed to swell for an hour, and dissolved by placing the containing vessel on a water bath. It is filtered and kept at a temperature of 40–50° C. (113–122° Fahr.).

Well-sized, hard-surfaced paper is cut into sheets, which are immersed one after another in a dish of water. A thick glass plate is meanwhile levelled, and a well-wetted sheet laid thereon : a piece of sheet rubber is laid over it, and the two squeezed together. The rubber is removed, and the edges of the paper are turned up all round about half an inch. The warm gelatine solution is poured into a tray thus formed, and by tilting the glass plate and with

the help of the finger or a brush, spread over the whole surface. This done, the plate is set aside in a horizontal position and a second paper coated, the first being dried as soon as the gelatine has set. The gelatinised papers are sensitised in—

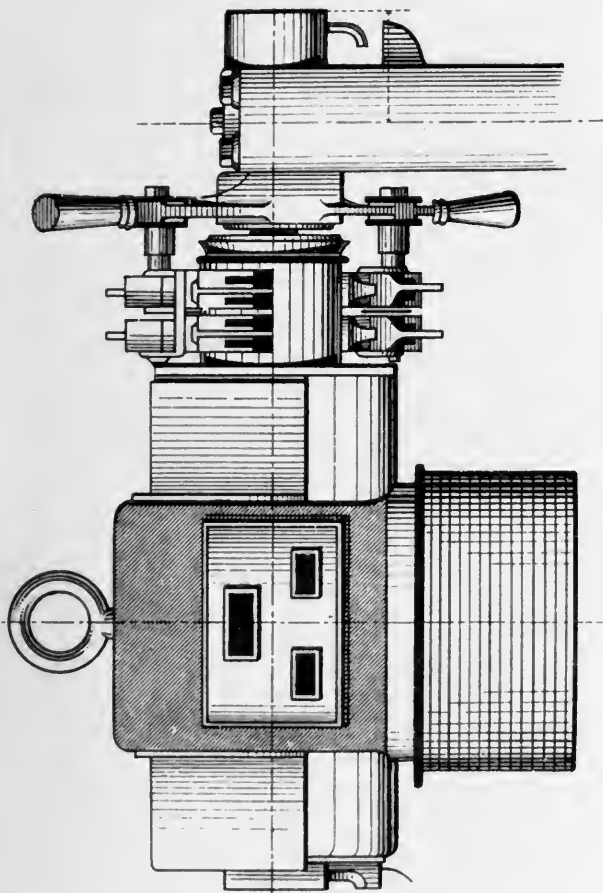
Potass bichromate, .	18 grains.	40 grams.
Water, . . . .	1 ounce.	1000 c.cs.

in which they are immersed for one or two minutes, any air bubbles being detached during that time with a camel's-hair brush. Sensitise in ordinary daylight, but dry in the dark: the paper keeps good for a week.

Exposure occupies about 20–25 seconds in bright sunlight, the design appearing as light yellow on a brown ground. Over-exposure can be corrected, but not under-exposure. The printed proofs are washed in several changes of cold water, as long as the soluble bichromate colors the solution yellow. Each proof is then separately dipped in a bath containing water at 28–30° Cent. (84°–88° Fahr.) for one or, at most, two minutes: this has the effect of slightly softening the lines of the drawing which the cold bath had brought into relief. The print is removed, laid face up on a level surface, and superfluous moisture blotted off. Fine pigment is now dusted over the paper from a fine gauze sieve and spread over the lines with a soft brush. It adheres to the lines, and should leave the ground white, but it usually happens that, owing to insufficient exposure, the ground is a little colored. Subsequent washing removes this. The pigmented copy is next dried in a warm place (in summer, in the

# BEMROSE'S CARBON PROCESS

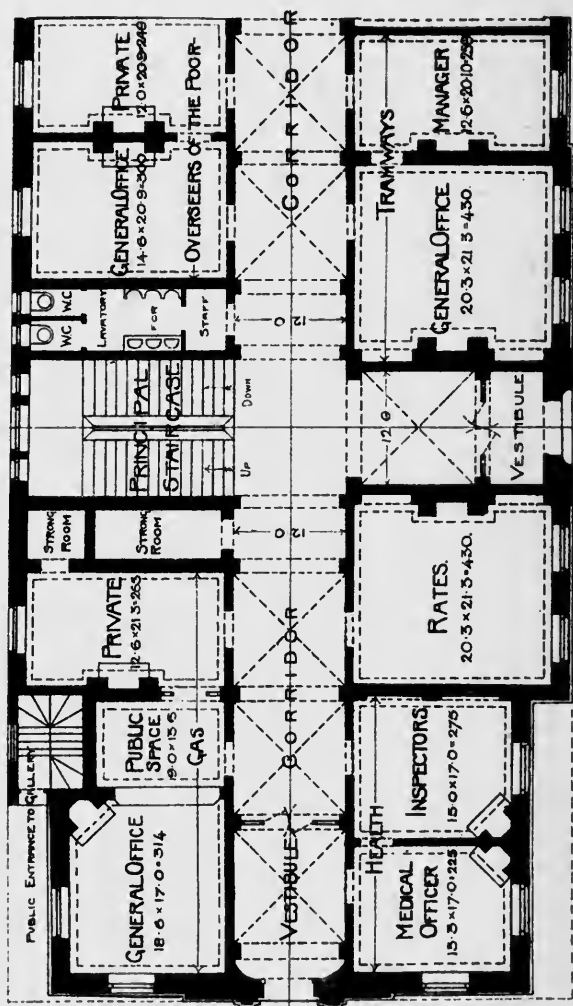
(Permanent).



Particulars on application to  
**BEMROSE & SONS, LTD.,**  
**DERBY. LEEDS & LONDON.**

# BEMROSE'S CARBON PROCESS

(Permanent).



Particulars on application to  
**BEMROSE & SONS, LTD.,**  
**DERBY, LEEDS & LONDON.**



sun ; in winter, near a fire or in a drying oven) at a temperature not above 60° C. (140° Fahr.). It is then soaked in cold water till limp, the ground cleared from superfluous color with a soft wet sponge, and finally, again dried. Many pigments can be used : vegetable black, ultramarine blue, gold and silver bronzes, all give good results.

*Abney's papyrographic process*, a form of collotype, depends on the fact that gelatine *plus* bichromate, on exposure to light, acquires the property of retaining fatty ink, and is specially suitable for taking a number of copies from one tracing. Stout paper is floated for two minutes on—

Potass bichromate, .	13 grains.	30 grams.
Gelatine, . . .	26 „	60 „
Water, . . .	1 ounce.	1000 „

It is hung up to dry and again floated, being this time hung up to dry in a position opposite to the first. Drying must take place in the dark.

After exposure the print is immersed in a dilute solution of alum to remove the greater part of the soluble chromate. It is then placed in a glass or zinc plate, and surface moisture removed with blotting-paper. It is then inked with lithographic ink, applied with a soft leather or velvet roller, and soaked in water till all soluble chromate is removed. The design is left in black lines on a white ground. From this print forty to fifty copies can be taken in an ordinary copying press, the print being inked for each impression.

*With Silver Salts.*—Papers (plain or albumenised)

sensitised with silver nitrate, chloride, or other salts, have been used for heliographic copying, giving a copy in white lines on a dark ground from an ordinary tracing. Those who wish to employ a silver process will find it better to use the commercial sensitised paper rather than to prepare one for themselves. The only use, however, to which present-day copyists are likely to put the process is in preparing the negative from a small tracing, from which to print positive copies on ferro-prussiate or albumenised paper.

Directions for working the process will be found in any of the larger treatises on photography.\*

Liesegang † describes a rapid silver paper—containing silver chloride and iodide and developed with gallic acid—which is capable of being utilised in everyday work to some advantage.

\* Abney's *Instruction in Photography*; Eder's *Handbuch der Photographie*. For sensitising formulæ and brief instructions, see also *The Figures, Facts and Formulæ of Photography*.

† *Die modernen Lichtpausverfahren*, p. 31.

## CHAPTER XVIII

## PRINTING HOUSE MEMORANDA

*To Oil Drawings on Paper for Printing.—*

Castor oil, . . . . .	3 parts.
Alcohol, . . . . .	10 „

Lay the paper face down on a glass plate and rub in the above solution with a small sponge. Warm before a stove to allow the oil to thoroughly soak in. When the paper has become transparent remove all superfluous oil with a clean rag or blotting-paper, and again warm. The paper can be restored to its original condition by soaking in alcohol once or twice, and then in water mixed with alcohol.

Another method is to iron paraffin wax into the warm and dry paper with a hot iron. Remove surplus wax by rubbing with a soft cloth.

*Potash Oxalate Solution for removing Stains.—*

Potass oxalate, 1 part.	75 grains.	170 grams.
Water, . . . . .	6 parts.	1 ounce. 1000 c.cs.

This solution at once removes the blue image from both ferro-prussiate and Pellet prints. The paper should be afterwards well washed : if this is not done, the blue color is very liable to reappear in course of time.

For use on a pen the solution is thickened with a little gum arabic, though, unless the draughtsman sends the copies back to the printing house to be again washed, he had better put in white lines on ferro-prussiate prints with Chinese white.

*Mounting Prints.*—To mount on linen, paste the back of the copy thoroughly well with fresh flour paste and leave for five or ten minutes. Tack the linen tightly to a smooth table and gently lower the pasted print upon it. Roll a duster round a piece of wood to make a firm but soft pad, and rub the paper into contact, working from the middle in all directions.

*To Varnish Mounted Copies.*—Give a coat of size (1 part of glue dissolved in 10 parts of water), and, when dry, varnish as evenly as possible with a good 'oak' or 'church' varnish.

*Sizes of Drawing Papers.*—

Demy, . . . .	17 × 22 inches.
Royal, . . . .	20 × 25 „
Cartridge, . . .	21 × 26 „
Double crown, . .	20 × 30 „
Imperial, . . . .	22 × 30 „
Double demy, . . .	22 × 35 „
Double elephant, .	27 × 40 „
Antiquarian, . . .	31 × 53 „

## CHAPTER XIX

## MANIPULATION

*Weights and Measures.*—Since making up solutions enters very considerably into the working of the processes described in these pages, the question of weights and measures may be appropriately mentioned under this heading. In almost every instance, both metric and English units are given, but the writer strongly advises the reader to work by the metric. A set of weights from 50 grams to 1 gram can be bought for one shilling and threepence. The fractional parts of the gram—.5, .3, .2, and .1—can be cut out of aluminium foil, or a second set from 10 grams to .01 gram only costs another eighteenpence. A 250 c.c. measuring cylinder costs about two and threepence, whilst a wide-mouth bottle of about 35 to 40 ounces capacity can be marked with a diamond for a litre measure, or a cylindrical litre measure bought for about five shillings.

The readiness with which large or small quantities of a solution can be at once compounded from the formula will convince the photographer of the superiority of the decimal over the English system.

*Hydrometers.*—When working on a large scale, particularly when chemicals (like ferric chloride) of

indefinite composition are being used, it is often advisable to adjust the strength of the solution by the hydrometer, as is done in the case of the Pellet sensitiser given on page 69. Hydrometers measure the specific gravity of the liquid, and are made to cover a certain range of specific gravity, say, 1·00–1·20, 1·20–1·40, and so on. They cost about half-a-crown each. The specific gravity of every liquid varies with the temperature, and it is therefore usual to adopt the temperature of 60° Fahr. (15°·5 C.) as that at which the gravity is to be taken. If the temperature of the solution differs more than a few degrees from this, the containing vessel is placed in warm or cold water, as required.

Baumé's hydrometer, which is much used on the Continent and in America, is differently graduated: its zero mark corresponds with specific gravity of 1·00. The following figures give the gravities equivalent to degrees Baumé:—

Baumé.	Sp. Gr.	Baumé.	Sp. Gr.
30	1·256	40	1·375
31	1·267	41	1·388
32	1·278	42	1·401
33	1·289	43	1·414
34	1·300	44	1·428
35	1·312	45	1·442
36	1·324	46	1·456
37	1·337	47	1·470
38	1·349	48	1·485
39	1·361	49	1·500

*Filtering.*—Many of the solutions specified in these pages require filtering, if spotless results are to be obtained, and as many readers may never have fitted a filter paper into its funnel, one or two words on the right way to do this are given here. A suitable filter paper is Rhenish, No. 597, made by Schleicher and Schüll, and obtainable at any chemical dealers in packets of 100 circular papers from

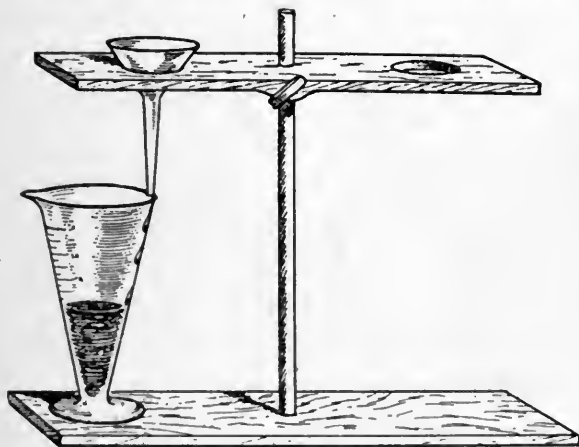


FIG. 14.—Filtration.

3 inches diameter upwards. The way in which the paper is fitted into the glass funnel has a good deal to do with the rapidity of filtration. First, fold the circular paper into two, and then again into four, making the last crease lightly. Place the paper in the dry funnel, and, gently placing the finger in the cone of the paper, see what amount of play is possible. The filter ought to 'waggle' to and fro

about a quarter of an inch. If the first folding does not give this, try again, laying down one edge of the semicircular paper a little short of the other and opening out the filter to form a cone of angle greater or less than  $60^\circ$  as required. Place in the funnel, and press down the three-fold side of filter, so that the single thickness of paper is pushed against the glass on the opposite side and the point of the filter is turned away from the three-fold side. Now, holding the funnel in

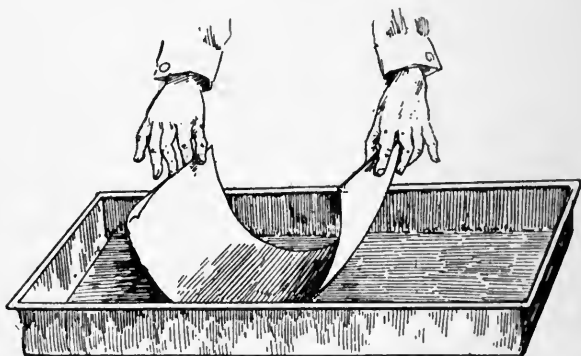


FIG. 15.—Coating Paper by Floating.

the hand, single paper lowermost, pour water into the filter on the single side, bring into the vertical position and, taking hold of the two sides of the filter at the points where the single and treble thicknesses meet, slightly lift up the paper. The stem will at once fill with water and filtration will proceed rapidly. Though taking some time to describe, the operation only occupies a few seconds.

*Coating Paper.*—This is done either by floating on the solution or by brushing the solution over the



paper. The latter method, inasmuch as it dispenses with large dishes and much solution, will commend itself to the photographer who only wants a small batch of paper. On the other hand, some solutions give a much more even coating by floating than by brushing.

(a) *By Flotation.*—To float the paper hold the sheet by opposite ends in a loop and gently lower the middle of the piece till it touches the surface of the liquid. By lowering the hand, the paper is gradually

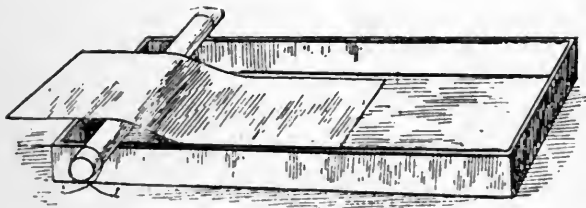


FIG. 16.—Withdrawing Paper after Coating.

brought on to the surface of the liquid so as to expel air bubbles (fig. 15).

When withdrawing the paper, a good plan is to lay a piece of glass rod across one end of the dish and to slowly draw the paper over it. This removes superfluous liquid as well as covers any minute air bubbles left after flotation (fig. 16). The time of flotation varies with different papers and baths and with the degree of impregnation desired. When one wants to keep the coating as much as possible on the surface of the paper, it is better to float for a short time, to dry, and refloat, rather than to expose the paper to a more protracted flotation.

(b) *By Brushing*.—Soft camel's or badger-hair brushes of good size are often used, but for many solutions the writer prefers a fine Turkish sponge or a piece of cotton-wool, clean and free from grit. A Blanchard's brush is another convenient tool. A piece of glass plate about  $6 \times 3$  inches has a strip of swansdown calico or Canton flannel folded over one end and secured with an elastic band (fig. 17).

After use, brushes and sponges should be well washed before being exposed to daylight. The cotton-wool and the material in the Blanchard brush are used fresh each time.

When applying the sensitising solution, it is almost



FIG. 17.—Blanchard's Brush.

always necessary to keep the brush or sponge only just wet enough to give a thin coating. Too much liquid on the paper means a flat sunken image. Give the paper steady, even strokes in one direction and then crosswise. Streaks must, of course, be avoided as much as possible, but it is not at all difficult to coat paper with satisfactory uniformity.

*Drying* in a proper manner is important. It should be quick, but the paper must not get hot, or fogged images may result. Some papers can be dried at a short distance from a fire, but it is more satisfactory to use a drying oven. This need not be at all an elaborate or expensive affair (for work on a small

scale), and below are given the figure and description of one, constructed on the lines of one described by Mr Alexander Cowan in the *Photographic Year Book* for 1881.

A box of suitable size is made, and a central aperture about  $2\frac{1}{2}$  inches diameter made in top and bottom. The upper aperture carries a length of stove piping in which, at about one foot above the box, a small Bunsen burner is fixed. A  $\frac{3}{8}$ -inch Fletcher's burner (price sevenpence without stand) answers well, and is screwed into a right-angled piece of tube, passing through the pipe. A small shutter is made in the pipe alongside the burner, for conveniently lighting the latter. To the lower aperture an inverted funnel-shaped vessel is attached, made of tin-plate and fixed by a flange to the under side of the box. From the side of this vessel a short length of stove pipe projects. The funnel is filled with fragments of asbestos, as used in gas fires. The interior of the box is provided with shelves of wood frames, covered with linen, on which the sensitive papers are laid to dry. These shelves are removable, and, if desired, the paper can be suspended to dry, by pinning it to a cross-piece of soft wood (about half-inch square section) and laying this on the supports of the top shelf. A hinged or sliding door is fixed to the front, and the whole is supported on four light iron legs, so as to leave the base of the funnel about twelve inches above the floor. An oil stove placed immediately below warms the air passing through the chamber containing the asbestos,

whilst the draught is increased by the burner in the chimney.

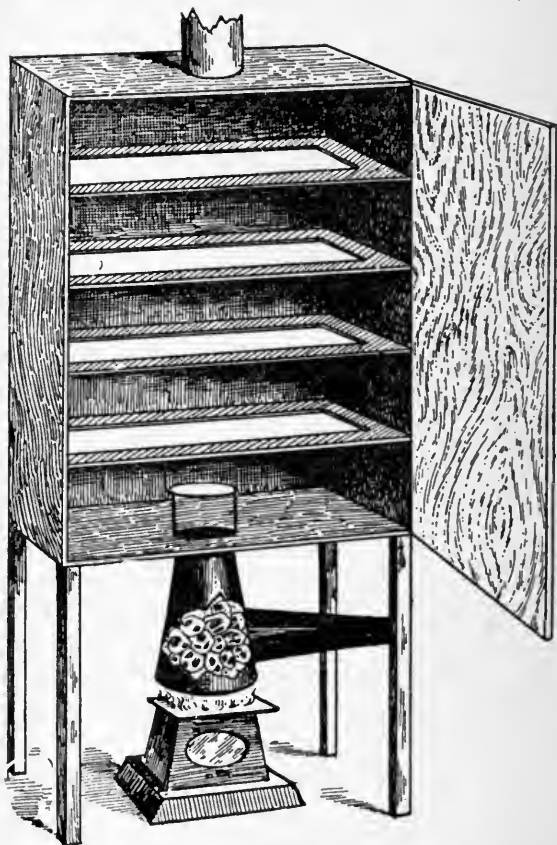


FIG. 18.—Drying Cupboard.

The air enters the cupboard on the right, passing through the chamber shown packed with asbestos balls, which are kept warm by the oil stove.

The use of the burner alone enables a current of cold air to be drawn through the apparatus. A very moderate increase in the temperature of the air is sufficient to make paper, coated by flotation or brushing, bone dry in half an hour.

*Storage.*—While the best results with almost all the processes here described are obtained on freshly prepared paper, it is often necessary to store it. Damp is the enemy of these papers, and, if they are to keep well, it must be excluded. A calcium chloride tube is the best receptacle, though it need not necessarily be of the form sold by the photographic dealers. Many household commodities are supplied in tins with almost hermetically sealing lids, and it is only necessary to divide off a small portion of the interior (to hold the calcium chloride) to have an efficient storage box.

To use calcium chloride to the best advantage it is mixed with asbestos. Soak commercial asbestos in a strong solution of the chloride, make the pasty mixture into little pats, and dry on the moderately warm part of the top of the stove. Gradually move to a hotter part, till the pats are dry right through, and store in a stoppered bottle for use. When these balls become damp they have only to be reheated on the stove to fit them for use again.

## CHAPTER XX

## PAPER AND SIZING

ONE of the advantages of the processes described in these pages is the facility with which the sensitising solutions can be applied to all kinds of papers, so that quite a variety of differently surfaced and tinted papers are placed at the photographer's disposal for printing purposes. The ferro-prussiate process can be worked with much commoner kinds of paper than others, such as Kallitype; but among good quality papers there is plenty of opportunity for the exercise of taste, and the newer school of pictorial photographers will no doubt find great possibilities in ringing the changes on tint of paper and color of image.

Among raw papers the well known brands of Saxe and Rives, long used for albumenised paper, need no introduction to the student of photography. They are sold in sheets  $18 \times 22$  inches, and can be used without additional sizing, though in almost every process a second sizing will do no harm, and will generally benefit the resulting paper as regards rapidity and brilliancy of image. Saxe and Rives paper can be obtained at some large photographic dépôts, and as the raw paper is not in very frequent demand it is as well to specify 'un-albumenised' when ordering it.

Whatman's drawing papers, supplied in three grades of surface, are very suitable both for large and small work. They are supplied in the various sizes used in drawing offices as given on page 116.

Some prices are here given as a guide to ordering:—

			Per sheet.		Per quire.	
			s.	d.	s.	d.
Demy,	.	HP, N.	0	1½	3	0
Royal,	.	HP, N, R.	0	3	6	0
Imperial,	.	HP, N, R.	0	5	9	9
„	thick,	HP, N, R.	0	7½	14	3
„	extra thick,	HP, N, R.	1	0	22	6
Double elephant,	.	HP, N, R.	0	10	19	0

The letters in column 2 indicate the surfaces in which each size is made. HP is hot pressed or smooth ; N, not pressed or natural grain ; R, rough.

Cartridge papers, too, are very suitable, and can be had in a variety of tones and sizes from large stationers such as George Gill & Sons, of Charterhouse Street.

Reeves & Son, and other artists' dealers, stock a few French drawing papers which are used for gum-bichromate work. The brands are, *Allonge*, *Canson* (18 different tints), *Michallet* and *Ingres* (5 tints). Of these *Michallet* and *Ingres* are papers of peculiar texture, and take the ferro-prussiate and Kallitype solutions very well : with the other two brands the writer gets degraded lights, though possibly the pictorial worker may sometimes be able to make effective use of this property.

Other artists' papers which have been found

suitable for photographic use are Wrigley's imperial amber antique rough surface boards, Dutch hand-made *Van Gelder* (obtainable in several textures from the London agents, Grosvenor, Chater & Co., Cannon Street, E. C.), and Japanese proof papers.\*

Albumenised paper (unsensitised, of course) takes the ferro-prussiate and other solutions perfectly, and gives very fine brilliant prints.

Better-class hard-surface writing papers may be used. A local stationer or printer will supply these.

For engineering purposes, where large tracings are to be copied, it is imperative to use a stout paper.

A common or thin paper means great risk of tearing the print during washing. Special tough, hard-surfaced papers are made for the purpose, in various degrees of stoutness—extra stout, stout, thin, and extra thin. The lighter kinds are suited for sending through the post, or for making copies to be subsequently used as negatives (page 102). The heavier brands stand the wear and tear of shop use better. They are supplied in rolls of 30 inches wide and upwards. Steinbach (London agents, Otto König & Co.) makes good brands suitable for the various heliographic processes.

While very cheap papers can be employed for blue printing, if well sized and used fresh, it should be borne in mind that, for a sensitive paper to keep, sizing must be reduced to a minimum. Hence a pure, hard-surfaced, close-grained paper becomes necessary, if the coated paper is to be kept any

\* E. Sanger Shepherd, *The Photogram*, 1896, p. 190 (Aug.).



length of time, but when it is convenient to use the paper within a few days of its being coated, it is quite easy to secure equally good results on much cheaper papers. Light-colored, heavy manilla wrapping paper, used for newspapers and magazines, can be used, with this qualification.

Reeves & Son supply a fabric (*Linaura*) resembling tracing cloth which takes the ferro-prussiate solutions quite well. It is practically untearable and uninjured by moisture, whilst the sensitised fabric is said to keep in good condition for a much longer time than similarly coated paper. It is sold in rolls 36 inches and 42 inches wide.

*Sizing* fills up the pores of the paper, keeps the image on the surface, and so prevents flat and sunken prints. Besides this, the presence of the organic body—gum, starch, or gelatine—probably acts in many instances as a 'sensitiser' of the sensitive compound, conferring greater sensitiveness upon the paper.

The most effective and, for the amateur, most convenient method of sizing is with arrowroot, as described by Duchochois.

Take—

Arrowroot,	.	.	9 grains.	20 grams.
Glucose,	.	.	2 „	5 „
Water,	.	.	1 ounce.	1000 c.cs.

Mix the glucose and arrowroot with a little cold water, add the remainder hot, and boil up the whole in a porcelain dish. A cheap methylated spirit lamp (fig. 19) is very convenient for this purpose,

and will be found very useful on many other occasions. An ordinary 'Granitine' developing dish can be used instead of the evaporating basin shown in the figure, though the latter is handier in use. Stir all the time heat is being applied, with a spoon or glass rod. As soon as the liquid boils extinguish the lamp and place the basin in a large dish of water to cool. Remove the skin from the surface, and strain through fine canvas.

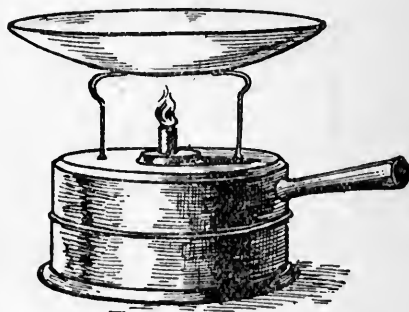


FIG. 19.—Spirit Lamp for making Size.

The necessary number of sheets of paper are nailed down by the four corners to a board about half an inch smaller each way than the paper. Obtain three soft Turkish sponges: rinse them in water: with one take up a little arrowroot solution, and, using it lengthways and crossways, spread the thin paste into an even layer. Then with the second sponge rub very lightly over the coating so as to spread it as evenly as possible. Take off any excess of paste with the third sponge.

*Gelatine Sizing.* —

Hard gelatine, . . .	150 grains.	9.5 grams.
Water, . . . . .	30 ounces.	850 c.cs.
Alum, . . . . .	45 grains.	3 grams.
Methylated spirit, . .	7 ounces.	200 c.cs.

Soak the gelatine in the water for half an hour, pour off the water into another vessel, and heat it in a water bath to 140° F. Then pour back over the gelatine, and when the latter is dissolved add the alum dissolved in a little water, and lastly the spirit; common methylated spirit precipitates mineral naphtha when mixed with water, so that, unless the unmineralised spirit can be used (and this is obtainable only in rather large quantities), absolute alcohol had better be substituted. Gently draw the paper into this solution, avoiding air-bells; soak for two or three minutes, dry quickly, re-immerses as before, and again dry, this time hanging up the paper by the two opposite corners.

Gum arabic—a few grains per ounce—can also be used as size, and is brushed over the paper.

‘Gloy,’ a commercial paste, makes a good size according to Mr. Thomas Manly, in a letter to the writer. It is neutral and keeps well.

## CHAPTER XXI

## CHEMICALS

THE ferric salts are the compounds chiefly used in the processes described in these pages, and some space may therefore be devoted to the preparation and properties of these and several other equally important substances.

*Ferric chloride* may be purchased in three forms : (1) anhydrous (sublimed) ; (2) crystallised or solid ; (3) in solution.

*The anhydrous salt* forms small dark green crystals, which absorb water from the air with the utmost readiness. Its cost is considerably greater than the other forms in which the salt is sold, but for use on a small scale it has the advantage of definiteness of composition so long as it is kept well stoppered.

*Crystal or solid ferric chloride* is sold in large yellow lumps also very deliquescent. Their composition corresponds approximately to  $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ , equivalent to very nearly 60 per cent. of anhydrous chloride. Whenever 'ferric chloride' is prescribed in a formula without further specification, it may be taken that this crystal form is meant.

*Solution of Ferric Chloride.*—Ferric chloride is a most soluble salt, and solutions up to syrupy

consistency can be prepared. A solution very much used in preparing heliographic papers has a specific gravity of 45° Baumé (=1.45, water=1). The ferric chloride liquor of the British Pharmacopœia (*liq. ferri perchloridi fortis*) has a specific gravity (1.42) very near this, and contains 286 grains anhydrous ferric chloride per ounce, or 653 grams per litre.

The following table, enlarged from *The Photogram*, 1894, page 139 (June), gives the gravities and strengths of ferric chloride solutions :—

Degrees Baumé.	Specific gravity.	Ferric chloride, anhydrous. Grams per 100 grams.	Ferric chloride, anhydrous. Grams per 100 c.cs.	Ferric chloride, cryst.* Grams per 100 c.cs.
48	1.501	49	74	127
45	1.454	47	68	118
43	1.426	45	64	111
40	1.384	41	57	98
38	1.359	39	53	91
36	1.334	37	48	85
33	1.298	34	44	76
30	1.264	31	39	68

*Ferric ammonium citrate* is purchased in thin, transparent scales of deep red color with a metallic-like lustre. It is soluble in half its weight in water to a clear brown solution. If the crystals are

\* Calculated on basis of 58 per cent.  $\text{Fe}_2\text{Cl}_6$ , as ascertained by analysis.

opaque, and the salt forms a blue solution on first dissolving in water, decomposition has taken place, and such salt is liable to yield paper which will not give pure whites.

The composition of the brown citrate is said to be  $4\text{FeC}_6\text{H}_5\text{O}_7 \cdot 3(\text{NH}_4)_3 \cdot \text{C}_6\text{H}_5\text{O}_7 \cdot 3\text{Fe}(\text{OH})_3$ .

*Preparation.*—When circumstances make it advisable to prepare the salt, the simplest plan is to follow the instructions of the British Pharmacopœia.

Add 16 ounces (320 c.cs.) of strong ammonia (sold as .880) to 40 ounces (800 c.cs.) of water. Add to this, little by little, 10 ounces (200 c.cs.) of ferric sulphate solution (B.P.) previously diluted with 40 ounces (800 c.cs.) of water. Stir well, and set aside for two hours, stirring occasionally. Filter on a calico or flannel filter, and wash the residual ferric hydrate with water till the washings give no more reaction for sulphate (on testing with a few drops of barium chloride solution) than the washing water itself. It would, of course, be better to wash in distilled water, but ordinary tap water will answer almost as well. Dissolve 4 ounces (80 grams) of citric acid in its own weight of water, and gently warm the solution on a water bath. Add the ferric hydrate (well drained) and stir together till nearly the whole of the hydrate has dissolved. Let the solution cool, add  $5\frac{1}{2}$  ounces (110 c.cs.) of ammonia, and filter through flannel, adding a little distilled water, if filtration proceeds too slowly. Evaporate till syrupy, and dry on porcelain or glass plates at a temperature not above  $100^\circ$  Fahr.

The green ferric ammonium citrate introduced by Valenta and supplied by Merck, is stated to have the composition  $5\text{FeC}_6\text{H}_5\text{O}_7 \cdot 2(\text{NH}_4)_3 \cdot \text{C}_6\text{H}_5\text{O}_7 \cdot \text{NH}_4\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ . \*

*Ferric oxalate* can be bought crystallised, but is expensive. It occurs in small, pale-bluish green crystals which do not dissolve readily in cold water, but very readily in hot, without depositing when the solution cools. The salt and its solution should be kept in the dark.

Ferric oxalate is easily made from a ferrous or ferric salt, and the writer gives below the process and quantities of chemicals required for 100 grams of ferric oxalate in 20 per cent. solution. The reader who wishes to use English weights and measures must substitute for grams some English unit throughout—grains, drachms, or ounces, according to the quantity he requires.

Iron alum or ferric chloride solution is the simplest raw material for the manufacture of ferric oxalate. If ferrous sulphate is used the following preliminary treatment is necessary.

150 grams (theory, 148) of protosulphate of iron are dissolved in hot water, a little sulphuric acid added, and then, very cautiously, about 15 c.cs. of strong nitric acid (sp. gr. 1.4). The liquid must be in a porcelain basin. Enamelled iron might, with some risk, be used. The first addition of the nitric acid produces a dark brown color. As the acid is added its action becomes more energetic, and at the

\* *Photographische Korrespondenz*, 1897, p. 77.

end of the process (which may be thus recognised) the liquid bubbles up, giving off red fumes and becoming clear orange-red in color. A little more nitric acid is then added, and the liquid allowed to cool. From this stage the solution which contains ferric sulphate and nitrate is treated exactly as the iron alum or ferric chloride solution to be now described.

256 grams iron ammonium alum, or 132 c.cs. ferric chloride solution (B.P., sp. gr. 1.42), are diluted with water to about 1000 c.cs. and poured into 100 c.cs.



FIG. 20.—Filter for washing Ferric Hydrate.

strong ammonia diluted to a like amount. The alkaline liquid may be contained in a clean tin vessel. The precipitated ferric hydrate is allowed to settle, the clear liquid syphoned off, and some boiling water stirred up with the residual precipitate. The whole is then poured on to a flannel or calico filter (fig. 20) and washed for several hours in a current of cold water, being occasionally well stirred up on the filter with a piece of glass rod, rounded at the

end, or a silver spoon. As much as possible of the liquid is squeezed out of the flannel, and the precipitate scraped out with a silver spoon into a porcelain basin.

All the foregoing operations may be performed in



broad daylight. The remaining part of the process must be conducted in a dark room.

100.5 grams of finely powdered, pure oxalic acid are sprinkled over the precipitate, mixed up with it, the dish covered over and left to itself, save for occasional stirring, for a day or two. The process of solution may be hastened by heating to not above 85° Fahr.: for this a small oil stove placed some distance below the dish answers well. Test the temperature with a thermometer; if it goes much above 85° Fahr., the salt is partly reduced to ferrous oxalate. The solution gradually turns from pure green, through yellowish-green, to greenish-brown. This strong solution must be diluted with distilled water till it measures 500 c.cs. 10 c.cs. then contain 2 grams: it will keep indefinitely in a cool and dark place.

*Potassium ferrocyanide* (yellow prussiate of potash) occurs in large lemon-yellow crystals, sometimes turbid or translucent (not a sign of impurity). The salt keeps well, exposed to light and air, has a neutral reaction, and is not poisonous. The saturated solution (at 60° Fahr.) contains 259 grams per litre and has a specific gravity of 1.14.

*Potassium ferricyanide* (red prussiate of potash) forms fine, large, blood-red crystals which, when the salt is pure and fresh, are transparent. The powdered salt is orange-red. Exposed to light, both in the solid state and in solution, it is decomposed with formation of ferrocyanide and of a blue precipitate. It is therefore very important to store the solution (well stoppered) in the dark and to rinse

crystals, which are not clear ruby red, with a little water—drying them between blotting-paper—before weighing them. The concentrated solution is brownish-yellow; the weak, lemon-yellow. 100 parts of water dissolve nearly 40 parts of the salt at ordinary temperature.

*Uranium acetate, nitrate and chloride* resemble one another in their general properties. They are all very soluble in water,—50 parts in 100 parts of water.

*Gallic acid* ought to be nearly white needles, but is often of a brownish tinge. One part dissolves in 130 parts of cold water, 3 parts of boiling water, 12 of glycerine, and 5 of alcohol.

*Tannic Acid*.—Light brownish powder of thin glittering scales. It is very soluble in water, alcohol, or glycerine. One part of either of these solvents dissolves one part of the acid.

*Gum arabic* is nearly colorless, but often has a yellowish tint: it should be nearly inodorous. It is insoluble in alcohol and very soluble in water, forming a translucent viscid solution, which is thickened or rendered turbid by ferric salts. The price of gum arabic varies from two shillings to four shillings and sixpence per pound, according to its purity. One of the best brands is 'White Senaar,' another 'Senegal.'

## CHAPTER XXII

## CHEMISTRY

*Ferrous and Ferric Salts.*—There are two series of salts of iron—the ferrous and the ferric. They differ in the proportion of oxygen (or other negative element, such as chlorine) which they contain. Ferrous chloride,  $\text{FeCl}_2$ , may be taken as typical of the ferrous series, and ferric chloride,  $\text{Fe}_2\text{Cl}_6$ , of the ferric series. It is quite easy, by chemical means, to convert any member of one series into the corresponding member of the other. Thus, reducing agents, substances like sulphurous acid, which readily combine with (and remove from any compound) oxygen, chlorine, or similar electro-negative elements, convert ferric salts into ferrous; whilst oxidising agents, substances like nitric acid or potassium permanganate, which readily supply oxygen, chlorine, or similar elements to any compound, convert ferrous salts into ferric salts.

*Chemical and Photo-chemical Reduction of Ferric Salts.*—The above chemical reactions go on irrespective of the action of light, though heat is sometimes necessary to start or complete them. There are, however, certain reducing agents which convert ferric into ferrous salts only under the influence of

light. For instance, a solution of ferric chloride in ether remains quite unaltered in the dark, but on exposure to sunshine soon loses its yellow color and becomes reduced to ferrous chloride, the change being accompanied by the decomposition of a portion of the ether.

Paper, too, saturated with a solution of ferric chloride and dried, is similarly capable of effecting the reduction of the ferric salt. These changes—not merely chemical, but photo-chemical—are examples of many which take place not in the case of salts of iron only, but of compounds of uranium, cobalt, manganese, chromium, and other metals.

There is one distinguishing feature common to the bodies which undergo photo-chemical decomposition in this way—or at any rate to those of which any practical use can be made. They are all compounds of elements which, like iron, are capable of existing in two states of oxidation. It is generally only the more highly oxidised compounds which are sensitive to light, the decomposition resulting in the formation of a salt of a lower degree of oxidation, and in order that photo-chemical action shall take place, it is necessary that the metallic salt shall be associated with a mild reducing agent such that when exposed to light, the reduction of the ferric (or other) salt and the oxidation of the reducer shall go on together.

If the reducer is too powerful, decomposition takes place without the aid of light at all (ferric chloride and sulphurous acid): if no compound is present which can take up the oxygen or other element from the compound exposed to light, no photo-decomposi-

tion takes place (ferric chloride in aqueous solution) : whilst the case of ferric chloride in ethereal solution is an example of the principle just cited, of exposing a substance in the presence of a second, capable of promoting its decomposition in the light.\*

This reducing matter need not necessarily be a separate compound : it may be combined with the ferric salt, as when organic salts of iron (oxalate or citrate) are made use of.

The chief compounds of which practical use has been made are the ferric and the alkaline bichromates, and the processes which have been developed depend on the differences in the behaviour of various reagents towards these salts and their lower compounds. For example, ferrous salts reduce the noble metal from compounds of platinum or silver, whilst no such action is exerted by the ferric salts—a difference which is the basis of the platinotype and Kallitype processes.

*Action of Light. Ferric Salts.*—The ferric salts of mineral acids (such as sulphuric, hydrochloric) are reduced to the corresponding ferrous salts when exposed to light with various organic bodies, such as oxalic acid, citric acid, tartaric acid, gelatine, gum, etc., whilst a similar change takes place in the case of organic salts of iron like the oxalate, tartrate, and citrate. Very often the use of a double salt of iron and ammonia gives better results, and the reason ascribed is that the ferric salt possesses the property of dissolving the newly formed ferrous salt to such an extent as to weaken the vigour of the image. The

\* See *Chemistry of Photography*, by Raphael Meldola, Macmillan, 1891, pp. 12-20 and 71-82.

introduction of ammonia into the compound counteracts this solvent action, and hence ferric ammonium citrate, ferric ammonium oxalate, etc., are compounds which are very frequently used in preference to the simple iron salts.

*Uranium Salts.*—The metal uranium forms two series of salts—the uranic (yellow solutions) and uranous (green solutions). The salts most used are uranic nitrate, chloride, and acetate, though the organic salts of uranium offer a promising field for experiments. On exposure to light, uranous oxide,  $\text{UO}_2$ , and the uranous salt of the acid are generally produced.\*

*Chromium Compounds.*—Exposed to light in contact with organic substances such as gum, gelatine, etc., alkaline bichromates ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) become reduced to chromium salts, whilst the associated organic matter has several of its physical properties modified. Both of these changes are utilised in one process or another for the production of an image.

Thus, the unaltered chromate reacts with silver nitrate, giving a red precipitate of silver chromate, whilst the reduced chromium salt does not; but the most important processes are those dependent on the alteration of the gum or gelatine. The principal changes are in (1) solubility, (2) hygroscopic properties, (3) power of imbibition (or ability to absorb water).

(1) Gelatine or gum, mixed with bichromate, and exposed to light, becomes insoluble in hot water, a

\* *Vide* Burnett's "Researches," *British Journal of Photography*, 1857 and following years.

change which is the basis of the well-known carbon and similar processes.

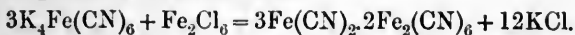
(2) Bichromated gum or dextrine is tacky before exposure to light, but after exposure is found to have lost this property, so that a fine powder does not adhere to the exposed portions (*anthrakotype* and other 'powder' processes).

(3) Bichromated gelatine, exposed to light, loses its power of swelling by absorption of water, and if a gelatine surface, some parts of which have been exposed and others not, be immersed in cold water, and a roller, charged with greasy ink, then passed over it, the ink is repelled from the unexposed portions, but adheres to the unswollen portions (basis of *papyrotype*, page 113, *heliotype*, and other processes).

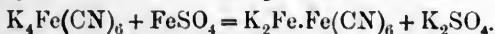
As explained above, all these printing processes with metallic salts—to use a long phrase for what the Germans call *Lichtpausverfahren*—depend on the difference in action of certain reagents on the salts and on their products when exposed to light.

The principal reagents are potassium ferrocyanide, potassium ferricyanide, gallic and tannic acids, and silver nitrate. By referring to the reactions given below, the student will be able to understand the theory of the processes described in these papers.

**POTASSIUM FERROCYANIDE. Ferric Salts.**—Deep blue precipitate of Prussian blue.



**Ferrous Salts.**—Bluish white precipitate, which rapidly becomes blue on exposure to the air.



*Uranic Salts.*—Red-brown precipitate.

*Uranous Salts.*—Red-brown precipitate.

POTASS FERRICYANIDE. *Ferric Salts.*—No precipitate: merely a brown coloration.

*Ferrous Salts.*—Deep blue precipitate of Turnbull's blue,  $\text{Fe}_3\cdot\text{Fe}_2(\text{CN})_{12}$ .

*Uranic Salts.*—No precipitate.

*Uranous Salts.*—Red-brown precipitate of uranous ferricyanide.

TANNIC ACID. *Ferric Salts.*—Intense bluish-black precipitate.

*Ferrous Salts.*—In strong solutions a white gelatinous precipitate: none in weak solutions.

*Uranic Salts.*—?

*Uranous Salts.*—Red-brown precipitate.

SILVER NITRATE. *Ferric Salts.*—No reaction.

*Ferrous Salts.*—Precipitate of metallic silver.

*Uranic Salts.*—No reaction.

*Uranous Salts.*—Precipitate of metallic silver.

*Alkaline Chromate.*—Red precipitate of silver chromate.

*Chemistry of Prussian Blue.*—It would be out of the scope of this work to discuss the chemical constitution of the several varieties of Prussian blue. The student should refer to an article by W. Dittmar,\* where the chemistry of the question is discussed. But some of the chemical and physical qualities of these blues are of practical importance from the present point of view.

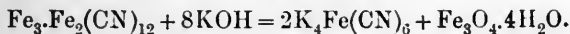
On exposure to bright light Prussian blue fades a

\* Thorpe's *Dictionary of Applied Chemistry*, vol. i. p. 640.



little, and regains its original intensity of color in the dark.

Caustic and carbonated alkalies (caustic soda and washing soda) decompose it, separating a hydrated oxide of iron and forming a soluble ferrocyanide—



The same result is produced, though much more slowly, by solutions of carbonate of lime and of magnesia; and as these salts are the almost invariable constituents of ordinary drinking waters, the point is of practical importance. If washed too long, the blue image is very considerably weakened.

Silver nitrate and mercuric sulphate act very powerfully on Prussian blue, destroying the blue color: the latter salt forms cyanide of mercury and sulphate of iron.

Oxalate of potash immediately decolorises and dissolves Prussian blue: so does cuprous chloride (subchloride of copper) dissolved in weak hydrochloric acid.

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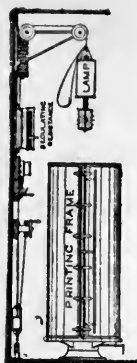
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# INDEX.

---

- ABNEY'S papyrographic process, 113.  
 Aniline process (Willis's), 105.  
 Anthrakotype, 111.
- BATHS, washing and developing, 85.  
 Blue paper, 11, 59, 90.  
 Blue prints, over-printed, 92.  
     ,, under-printed, 93.  
 "Blue solving," 115.  
 Bolle's toning process, 19.  
 Brewerton, W. E., color prints, 29.  
 Brown line (sepia) paper, 40, 73, 102.
- CARTER'S process (prints in dyes), 54.  
 Catechu toning, 17.  
 Chromate pigment processes, 107.  
 Coating, 13, 120.  
 Coating machinery, 62.  
 Color photography, Ferro-prussiate in, 29.  
 Cyanofer, 57.
- DRAWING papers (sizes), 116  
 Drying copies, 86.  
     ,, paper, 62, 122.  
 Dyes, prints in, 54.
- ELECTRIC light for printing, 79.
- Engineers, processes for, 56.  
 Exposure, ferro-gallic paper, 99.  
     ,, ferro-prussiate, 90.  
     ,, Pellet paper, 94.
- FABRICS, prints on, 53.  
 Ferric oxalate, making, 136.  
 Ferrogallic, 70, 99.  
 Ferro-prussiate, 11, 59, 90.  
 Filtering, 118.  
 Floating paper, 121.
- HARGREAVES' process (prints in dyes), 55.  
 Hydrometers, 117.
- INTENSIFYING blue prints, 22.  
 Iron pigment process, 106.  
 Itterheim's process, 108.
- KALLITYPE, 32.  
 Kallitypes, reducing, 39.
- LINAURA fabric, 129.  
 Long tracings, printing, 83.
- MACHINES for coating, 62.  
 Mafeking, blue prints at, 23.  
 Monsell's salt, 21.  
 Mounting prints, 116.
- "NEGATIVE" processes for engineers, 56.

- Newspaper work, blue prints, 28.  
 „ „ Kallitype, 43.
- OBERNETTER process, 45.
- Oiling drawings, 115.
- PAPERS, raw, 126.
- Papyrographic process, 113.
- Pellet paper, 57, 68, 94.
- Pigment processes, 106.
- Poitevin's process, 106.
- “Positive ferrotype,” 57.
- “Positive” processes for engineers, 56.
- Postcards, blue prints as, 24.
- Printing by electric light, 79.  
 „ frames, 77.  
 „ house, 88.
- REDUCING blue prints, 22.
- Register, negative, 23.
- Removing lines from blue prints, 115.
- Reynolds' formulæ, 15.
- Roy's toning process, 17.
- SEPIA paper, 40, 73, 102.
- Silver processes, 113.
- Sizes of drawing papers, 116.
- Sizing paper, 129.
- Spaulding's printing machine, 83.
- Stains, removing from blue prints, 115.
- Storage of papers, 125.
- TONING blue prints, 17.
- Tracings, making, 75.
- Transparencies, blue-print, 24.
- Transparent, making drawings, 115.
- Tri-color work, ferro-prussiate in, 29.
- URANIUM salts in ferro-prussiate, 15.
- Uranotype process, 49.
- VALENTA's formula, 14.
- Varnishing prints, 116.
- Vertical washing trough, 87.
- WATER for washing blue prints, 89.
- Weights and measures, 117.



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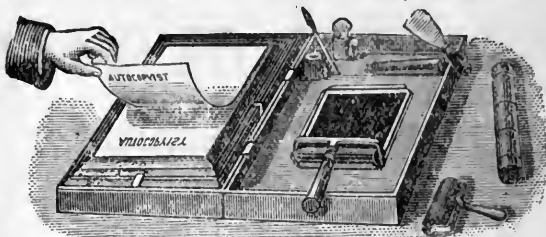
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